1993

Volatilization and bioremediation potential of soil contaminated by petroleum products

Seon-Hong Kang
Iowa State University

Order Number 9413989

Volatilization and bioremediation potential of soil contaminated by petroleum products

Kang, Seon-Hong, Ph.D.

Iowa State University, 1993

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Volatilization and bioremediation potential of soil contaminated by petroleum products

by

Seon-Hong Kang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Civil and Construction Engineering
Major: Civil Engineering (Environmental Engineering)

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1993

DEDICATION

To my father and mother, thank you for your sincere sacrifice and love!

TABLE OF CONTENTS

ACKNOWLEDGMENTS

I would like to express my sincere gratitude to Professor Charles S. Oulman. His guidance, encouragement, patience and support have made this research possible.

I also would like to express thanks to committee members who guided this research: Dr. Kenneth L. Bergeson, Dr. Alan A. Dispirito, Dr. Ladon C. Jones, Dr. Anthony L. Pometto III, and Dr. Thomas, D. Wheelock.

I appreciate the professors in my country who had guided my master's thesis: Dr. Chung-Hyun Park and Dr. Tae-Hack Chung.

I have a great gratitude to parents-in-law for their encouragement and love: Young-Sik Kang and Won-Im Cho.

I also would like to thanks to my fellow Korean students in this department for their warm advice and encouragement: Seung-Hyun Kim, Lim-Seok Kang, and Koo-Yul Chong.

Finally, I want to express the sincere gratitude to my wife, Hye-Jeong Kang for her sacrifice and love.

To my God, thanks you for this accomplishment!

1. INTRODUCTION

Leaking underground storage tanks are recognized as a major source of soil and water contamination (Donaldson et al., 1992). Of the 1.4 million buried gasoline storage tanks in use in the United States, about 80 percent are bare steel tanks lacking corrosion protection. A study of existing tanks by the US Environmental Protection Agency (USEPA) found that 35 percent leaked under test conditions with an average range of leakage of 29 L/day.

The most commonly applied cleanup technologies for soil contaminated by leaking underground storage tanks includes excavation of the soil and either incineration of the contaminated soil or burial in a landfill. Both of the disposal methods are very expensive when large volumes of soil are involved. Bioremediation is a safe and potentially economical alternative treatment that would permit reuse of the soil.

Prior studies at Iowa State University (Sajjad, 1992) tend to indicate that petroleum products such as gasoline, diesel fuel, and crude oil can be removed from soil by bioremediation. These same studies provided evidence that highly volatile products such as gasoline were also removed by volatilization. Gas chromatographic (GC) analyses were performed on a sample of gasoline contaminated soil that had not been treated with the bioremediation agent. At 15^{o}C, about 86 percent of the gasoline was removed by volatilization over a period of 21 days (or less) and at 35^{o}C the removal was about 97 percent.

The purpose of my research was to investigate volatilization as a competing process for the removal of fuels with bioremediation. If the rate of removal by

volatilization is fast enough, biological processes might make a small contribution to the overall removal that is observed. If the rate of removal by volatilization is slow enough, biological processes can make the major contribution to the overall process.

Based on the prior studies at Iowa State University (Sajjad, 1992), there was evidence that gasoline would be largely removed by volatilization and that diesel fuel would not. A variety of soil materials were used in the prior work but most of the laboratory studies have employed sand and gravel. Silica sand was selected as test material because it permitted to me to work with smaller samples in a hooded environment.

Several kinds of experiments were used to investigate volatilization. All were essentially gravimetric procedures in which the fuel loss from the sand was measured using an analytical balance. The results of these experiments provided a basis for modeling the volatilization process. One of the models was a material balance model developed as a part of this study. The other was a published model based on a heat transfer analogy. They are identical on a graphical form but the difference is in coefficients which they employ.

The model based on the heat transfer analogy did a very poor job of fitting the data whereas the material balance model fit the data very well. In addition to having value in predicting rates of volatilization, the material balance model explains why the rate of volatilization for gasoline is so much higher than it is for diesel fuel. Both models recognize that volatilization is driven by the vapor gradient that is developed in the pore space. The material balance model also accounts for the volatility of the fuel and the part it plays in establishing the path length over which the vapor gradient is established.

This study tends to demonstrate that respirometer studies employing gasoline contaminated sand were flawed by very high rates of volatilization of the gasoline. It is unlikely that carbon dioxide production was either enhanced or diminished by the gasoline

because it was removed so rapidly by volatilization. On the other hand, it is unlikely that our respirometer studies employing diesel fuel contaminated sand were flawed by volatilization. Bioremediation probably did account for diesel fuel removals and the robust carbon dioxide production probably does indicate that the diesel fuel is consumed along with other carbon sources in the bioremediation agent.

2. BACKGROUND

Gasoline is a complex mixture of refined petroleum hydrocarbons comprising more than 200 different compounds (Ridgway *et al.* 1990). According to the Merck Index (1989), gasoline contains C_4-C_{12} hydrocarbons. It can be obtained by fractional distillation of petroleum and contains mostly saturated hydrocarbons. The ordinary commercial grade contains paraffins, olefins, naphthenes, and aromatics. The average molecular weight of fresh gasoline is about 95 g/mole and that of weathered gasoline is about 111 g/mole. The average value of diffusion coefficient of gasoline in air is 4000 cm^2/day (Pedersen and Curtis ,1991). Some aromatic constituents of gasoline such as benzene are recognized carcinogens. Thus, gasoline spills pose a threat to the public health and groundwater resources.

Diesel fuel is a mixture of C_{10}-C_{12} hydrocarbons (Mackay, 1988). It is a middle distillate which boils within the range 170-390^oC. Diesel fuel is a mixture of alkane, alkene, and aromatic compound hydrocarbons. It is normally produced by blending two or more refinery streams such as light gas oil, heavy gas oil, and kerosene. About 15-30 % of diesel fuel is alkane hydrocarbons. Of the fuel oils used in terrestrial situations, diesel oil has the highest content of PAH (polynuclear aromatic hydrocarbons) and total aromatics (Wang *et al.* 1990). The average molecular weight is about 202 g/mole and the average value of diffusion coefficient in air is 4000 cm^2/day (Shields and Brown, 1989).

The most common toxic components in gasoline and diesel fuel are (EPRI, 1988):

Benzene	Pentane	*n*-Hexane
Ethylbenzene	1-Pentene	*o*-Xylene
n-Heptane	Toluene	Phenol

The major components of API PS-6 gasoline and their percent weights are summarized in Table 2.1. API PS-6 gasoline is a characterized gasoline used in petroleum research.

Gasoline and diesel additives other than the hydrocarbon groups will influence the behavior of gasoline and diesel fuel during their biodegradation process. Gasoline additives are used for anti-knocking, lead-scavenging, octane enhancement, metal deactivation, ignition control, icing inhibition, and corrosion inhibition, etc. Gasoline additives include cresyl phosphate, alkylamine phosphate, ethanol, methanol, isopropanol, MTBE, butyl phenol, etc. Diesel additives are used for detergency, smoke suppression, and improving flow and storage properties. Diesel additives include amines, amides, fatty acid succinimides, polyalkylene succinimides, polyalkylene amines, polyether amines, etc. (Sajjad, 1992).

Since petroleum products such as gasoline and diesel fuels and their additives contains many hazardous organic chemicals, their treatments are inevitable. A variety of physical and chemical treatments are now being developed and utilized (Table 2.2).

The most commonly applied cleanup technologies for soil contaminated by leaking underground storage tanks includes excavation of the soil and either incineration of the

Table 2.1. Major components of API PS-6

Compound	Percent Weight
2-Methylbutane	8.72
m-Xylene	5.66
2,2,4-Trimethylpentane	5.22
Toluene	4.73
2-Methylpentane	3.93
n-Butane	3.83
1,2,4-Trimethylbenzene	3.26
n-Pentane	3.11
2,3,4-Trimethylpentane	2.99
2,3,3-Trimethylpentane	2.85
3-Methylpentane	2.36
o-Xylene	2.27
Ethylbenzene	2.00
Benzene	1.94
p-Xylene	1.72
2,3-Dimethylbutane	1.66
Sum of other chemicals	43.75
Total	100

Reference: Parr *et al.*, 1991

Table 2.2. Available Physicochemical Methods for the Decontamination of Hydrocarbon-contaminated Soil

Methodology	Principles	Comments
Thermal	Evaporation and destruction of hydrocarbons	Excavation needed; top soils only; off-gases must be treated; expensive
Extraction	Removal of hydrocarbons into solution	Excavation needed; top soils only; extract must be disposed of; efficiency unknown; hydrocarbons may be bound to soils; very expensive; little data
Steam stripping	Removal of volatiles	Volatiles only; potential for subsoils; steam must be treated; little data
Hot-air stripping	Removal of volatiles	Volatiles only; potential for subsoils; little data
Chemical oxidation	Alteration of pollutant to ease removal	No information for hydrocarbons
Groundwater control	Pumping of aquifer to prevent flow	Prevents migration of hydrocarbons; no removal of compounds in unsaturated zone; efficient; useful to prevent pollution spread during biotreatment; widely used
Adsorption	Groundwater pumped through activated carbon	Expensive; waste requires disposal; efficiency unknown

Reference: Morgan and Watkinson, 1989

contaminated soil or burial in a landfill. Both of the disposal methods are expensive when large volumes of soil are involved. Bioremediation is a safe and potentially economical alternative treatment that would permit reuse of the soil (Thomas and Ward, 1989).

Many researchers have found that volatilization plays a role in bioremediation of volatile organic chemicals. Gersberg *et al.* (1991) conducted *in situ* bioremediation test of monoaromatic hydrocarbons in groundwater. They found that benzene, toluene, and xylene (BTX) were lost even in the control due to the physical losses such as volatilization.

Park *et al.* (1990) evaluated the fate of 14 polynuclear aromatic hydrocarbon (PAH) in soil under unsaturated conditions. They found that volatilization accounted for approximately 30 and 20 percent losses of naphthalene and 1-methylnaphthalene, respectively. For PAH compounds with greater than three rings volatilization did not play a significant role during biological process.

Anderson *et al.* (1991) conducted experiments on the fate, in soil, of a mixture of 15 volatile and semivolatile organic compounds commonly found at hazardous waste sites. They distinguished the abiotic losses from biological degradation over a 7-d period. They concluded that volatilization plays a significant role during biodegradation.

Volatilization fluxes were measured by Mayer *et al.* (1974). They first used the heat flow model to mathematically express the volatilization process of organic chemicals in the soil. However, this model did not fit my experimental data for petroleum products.

3. LITERATURE REVIEW

Volatilization can be defined as the loss of liquid chemicals into the atmosphere as a vapor (Spencer and Cliath, 1990). In other words, volatilization is the combined effect of "vaporization" and "diffusion"; liquid-phase chemical changes into vapor-phase by vaporization and vapor-phase chemical moves into atmosphere by diffusion.

Volatilization rates of organic chemicals from non-adsorbing surface are directly proportional to their relative vapor pressures. However, volatilization of organic chemicals from soil is more complicated because of many parameters affecting their adsorption, movement, and persistence. Organic chemicals in the soil volatilize at a reduced rate. The rate depends not only on the equilibrium distribution between the air, water, and soil matrix as related to vapor pressure, solubility, and adsorption coefficients, but also on their rate of movement to the soil surface by diffusion. Therefore, vaporization and diffusion will be separately investigated in this chapter. Several topics related vaporization, diffusion, and bioremediation of petroleum products in contaminated soil are discussed in this chapter.

3.1 Vaporization

Potential volatility of a chemical is related to its inherent vapor pressure, but actual vaporization rates depend on environmental conditions and all factors that control the organic compounds at the soil-air-water interface (Spencer and Cliath, 1990). Therefore,

vapor pressure and partitioning of organic compounds between soil-air-water interface are discussed in this section.

3.1.1 Vapor pressure

Vapor pressure is the force per unit area exerted by the molecules of a vapor in equilibrium with its pure liquid or solid form (Popendorf, 1984; CRC Handbook of Chemistry and Physics). The higher the vapor pressure for a given temperature, the more volatile the substance.

According to the kinetic theory, molecules in a liquid are in constant motion. This is an expression of their thermal energy (Hillel, 1971). Molecules collide frequently, and occasionally one or another absorbs sufficient momentum to escape from the liquid and into the atmosphere. The relative rates depend upon the concentration of vapor in the atmosphere relative to its concentration at a state of equilibrium (i.e., when the movement in both directions is equal). An atmosphere that is at equilibrium with free and pure liquid is said to be saturated. A liquid arrives at its boiling point when the vapor pressure becomes equal to the atmospheric pressure.

All solids and liquids possess a vapor pressure. It is a measure of the tendency of the substance to evaporate (Pedersen and Curtis, 1991). Conceptually, vapor pressure can be considered analogous to the solubility of the material in air at a given temperature. Higher vapor pressures reflect an increased tendency to volatilize.

Vapor pressure can be measured by the height to which the vapor can support a column of mercury. Therefore vapor pressure is often expressed in terms such as millimeters of mercury (mm Hg).

Volatilization is a process involving change of phase (Plimmer, 1976). The molecular arrangement within liquids is compact. The molecules in a liquid must acquire sufficient energy to overcome cohesive forces before they can leave the surface and become vapor molecules. The tendency of an organic compound to volatilize is expressed by its vapor pressure.

At a given temperature the vapor pressure of any substance is uniquely defined. This follows as a consequence of the phase rule. The system possesses one component and two phases (liquid and vapor) and one degree of freedom is possible. Therefore, vapor pressure is solely a function of the temperature for any substance.

If a liquid is contained in a closed vessel, the space above will be filled by vapor. Evaporation of the liquid will continue until equilibrium is achieved at a given temperature. From the standpoint of the assumptions of the kinetic theory of gases, at equilibrium the number of molecules leaving the surface (evaporating) is equal to those returning (condensing) and will be a function of their energy (temperature).

Vapor pressure is closely related to vapor density and can be calculated from it using the relationships:

$$\text{Vapor density} = \frac{W}{V} \text{ where } V \text{ is the volume of W grams of gas}$$

$$\text{Vapor pressure P} = \frac{W}{V}\frac{RT}{M} \quad \text{for an ideal gas}$$

where R is the molar gas constant,

T is the absolute temperature,

M is the molecular weight, and

V is the volume of weighed gas.

The vapor pressures of organic materials are important in predicting their behavior and fate when they are introduced into the environment (Grain, 1982). When a chemical has been spilled, for example, its approximate vapor pressure is needed to estimate its rate of evaporation. The persistence of chemicals that have been absorbed in the soil is also dependent on vapor pressure.

The equation that relate vapor pressure to temperature is commonly derived by integration of the Clausius-Clapeyron equation

$$\frac{d \ln P_{VP}}{dT} = \frac{\Delta H_V}{\Delta Z R T^2} \tag{3.1}$$

where P_{VP} is the vapor pressure in atmosphere,

ΔH_V is the heat of vaporization in cal/mol,

R is the gas constant in cal/mol*K,

T is the temperature in K, and

ΔZ is a compressibility factor, given by

$$\Delta Z = \frac{P_{VP} \Delta V}{RT} \tag{3.2}$$

where ΔV is the volume difference between vapor and liquid.

In Eq. 3.2, R has the units cm^3-atm/K, hence ΔZ is dimensionless and has a value of 1 for an ideal gas.

The simplest equation that can result from integration of Eq. 3.1 is

$$\ln P_{vp} = A_1 - B_1/T \tag{3.3}$$

where A_1 and B_1 can be expressed in terms of the parameters in Eq. 3.1. Equation 3.3 is the result obtained when $\frac{\Delta H_v}{\Delta Z}$ is assumed to be constant with changes in temperature.

Another mathematical expression for the vapor pressure is the Antoine equation:

$$\ln P_o = A - \frac{B}{T+C} \tag{3.4}$$

The addition of the third coefficient not only allows an expansion of the applicable temperature range but also permits greater accuracy within any given temperature range. These equations are applicable only within a specified temperature range. Extrapolation should be avoided.

The standard Reid apparatus is commonly used to measure the vapor pressure of compounds (Goodger, 1975). It consists of a sealed bomb made up of a fuel chamber connected to an air chamber of four times the volume, and fitted with a pressure gauge (Figure 3.1). The bomb is heated in a water bath controlled thermostatically to 100° F

(37.8° C). When equilibrium conditions have been established, the vapor pressure is read off the gauge, and corrections made for ambient pressure, and for the pressure rise of the air and water vapor initially present in the air chamber. An absolute value results, despite the use of the gauge, since atmospheric pressure is exerted both inside and outside the bomb at the commencement of the test. Vapor pressures of some organic compounds in gasoline are shown in Table 3.1.

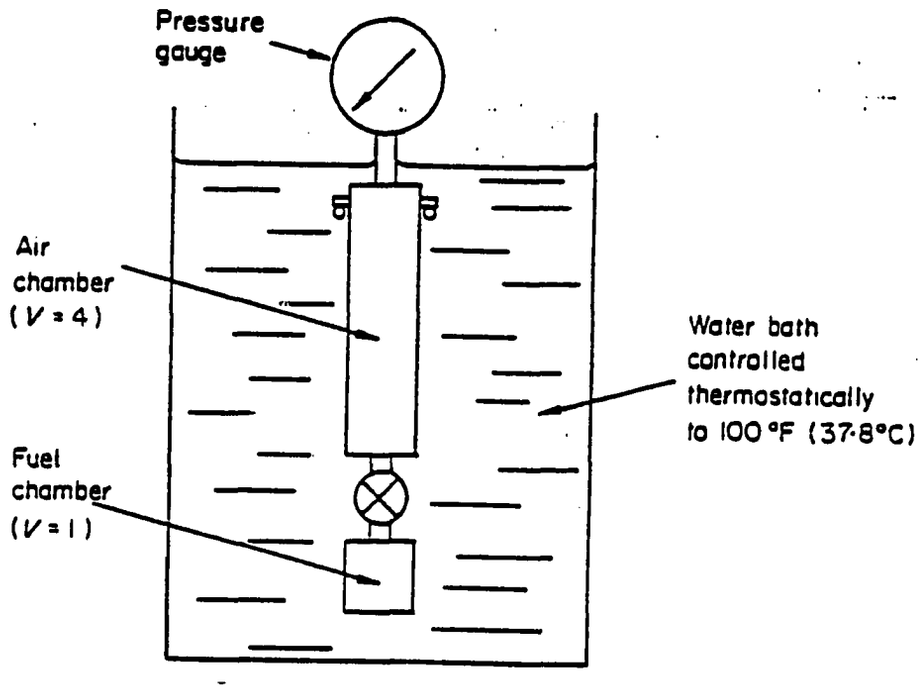


Figure 3.1. Sketch of Reid vapor pressure bomb (Goodger, 1975)

Table 3.1. Vapor pressures of some organic compounds in gasoline

Compound	Vapor pressure Pa, at 20°C
Benzene	1.01×10^4
n-Heptane	4.67×10^3
Toluene	2.93×10^3
m-Xylene	7.99×10^3
n-Nonane	4.29×10^2
n-Propylbenzene	3.33×10^2
1,2,4-Trimethylbenzene	1.33×10^2
n-Butylbenzene	1.33×10^2
1,2,4,5-Tetramethylbenzene	1.33×10^2
n-Dodecane	40

Reference: Donaldson *et al.*, 1992

3.1.2 Phase Partitioning of Organic Compounds

Organic chemicals may reside in either the vapor, liquid, or adsorbed phase. Thus, it is important to know how a given quantity of applied chemical will partition between three phases in the soil (Jury *et al.*, 1983). Vapor density of organic compounds are greatly decreased by their interactions with soil, mainly due to adsorption (Spencer and

Cliath, 1990). The reduction in vapor density due to adsorption depends on soil water content, the nature of organic compounds and its concentration, and soil properties, particularly soil organic matter content.

Partitioning between the soil and the water usually follows the linear or Freundlich equation, and the concentration of the desorbed organic compounds in the soil water is related to the vapor density by Henry's law. Thus, soil water adsorption coefficients can be used to calculate vapor densities in the soil atmosphere (Denahan *et al.*, 1990).

Organic compounds may move by molecular diffusion in soil in the vapor phase and in the solution phase. The relative importance of vapor phase and solution phase diffusion is determined by the relative magnitude of the concentration in air (vapor density) and the concentration in solution phase. Organic compounds whose partition coefficient between the soil water/ soil air is much less than 10,000 will diffuse mainly in the vapor phase and those whose partition coefficient in higher than 10,000 will diffuse primarily in the solution phase (Karimi *et al.*, 1987).

The liquid-vapor partitioning is generally represented through Henry's law,

$$C_G = K_H C_L \tag{3.5}$$

where C_G is concentration of organic chemical in the vapor phase (g / m^3 soil air)

C_L is concentration of organic chemical in the solution phase (g / m^3 soil solution)

and K_H is Henry's law constant which is dimensionless.

The Henry's law constant may be calculated as the ratio of saturated vapor density C_G^* (g / m^3) to organic chemical solubility C_L^* (g / m^3) (Jury *et al.*, 1983):

$$K_H = C_G^* / C_L^* \tag{3.6}$$

Adsorption reduces the chemical activity below that of the pure compound and affects the vapor density and the volatilization rate. Sorption may be a result of chemical adsorption (coulombic forces), physical adsorption (van der Waals forces), or hydrogen bonding. The concentration of the compound present in a desorbed state in solution in the soil water controls the vapor density of the compound in soil air. The vapor density is directly related to the volatilization rate (Thomas, 1982).

The linear and Freundlich isotherm equations have been most often used to describe organic chemical sorption on soils. These equations are given by,

$$C_S = K_D C_L \tag{3.7}$$

and

$$C_S = K_F C_L^N; \; N < 1 \tag{3.8}$$

where C_S is the adsorbed concentration of organic chemicals (g / kg soil)

C_L is concentration of organic chemical in the solution phase (g / m^3 soil solution)

K_D and K_F are the sorption coefficients or distribution coefficients, and

N is an empirical constant.

Values of K_D, K_F, and N are usually determined by curve-fitting sorption data obtained from batch equilibrium studies. The value of K_D or K_F is a measure of the extent of organic chemical sorption by the soil particles. The soil organic carbon (OC) content

can be used as a predictor of the sorption coefficient for non-ionic, hydrophobic organic chemicals. It has been reported that the sorption coefficient for a particular organic chemical, when normalized with respect to soil OC, is essentially independent of soil type (Wagenet and Rao, 1990). This has led to the definition of the OC-normalized sorption coefficient, K_{OC}, as

$$K_{OC} = (K_D \text{ or } K_F / \% \text{ OC}) * 100 \qquad (3.9)$$

When measured adsorption values are not available, reasonably good correlation has been found between K_{OC} and the octanol-water partition coefficient, K_{OW}. The correlation is expressed by following equation (Jury *et al.*, 1983):

$$\log (K_{OC} / 1000) = 1.029 \log (K_{OW} / 1000) - 0.18; \qquad (3.10)$$

$$r^2 = 0.91$$

K_{OW} (octanol / water partition coefficient) can be defined as follows (Lyman, 1982):

$$K_{OW} = \frac{\text{concentration in octanol phase}}{\text{concentration in aqueous phase}}$$

K_{OW} characterizes hydrophobicity of organic compounds. K_{OW} indicates the tendency for the compound to partition into soil organic matter. Compounds with high K_{OW} (e.g. >10) tend to sorb strongly to aquifer solids, which retards their movement. In

contrast, hydrophilic contaminants with low K_{ow}, such as ketones and alcohols, move freely in the subsurface (Bouwer and Zehnder, 1993)

The K_{ow} is not the same as the ratio of a chemical's solubility in octanol to its solubility in water, because the organic and aqueous phase of the binary octanol / water system are not pure octanol and pure water. At equilibrium, the organic phase contains 2.3 mol/L of water, and the aqueous phase contains $4.5 * 10^{-3}$ mol/L of octanol (Lyman, 1982).

In measuring the K_{ow} value, the chemical in question is added to a mixture of octanol and water whose volume ratio is adjusted to the expected value of K_{ow}. The system is shaken gently until equilibrium is achieved. Centrifugation is generally required to separate the two phases, especially if an emulsion has formed (Lyman, 1982). K_{ow} values for some organic compounds are shown in Table 3.2.

3.2 Diffusion

Diffusion is the movement of a component through a mixture under the influence of a concentration gradient which tends to move the component in a direction that will equalize the concentrations and destroy the gradient (McCabe *et al.*, 1985; Hillel, 1971).

At any temperature above absolute zero, the individual molecules of a substance move incessantly, randomly, and apparently independently of each other (Thibodeaux, 1979). Frequent collisions occur between particles, so that the path of a single particle is a

Table 3.2. K_{ow} values for some organic compounds

Compound	K_{ow}
Phenol	29
Toluene	490
o-Xylene	1100
Naphthalene	1550
Biphenyl	7760
Tetrachloroethylene	1050
Nitrobenzene	62
Chlorobenzene	692
Ethylbenzene	1100
Trichloroethylene	204

Reference: Ince and Inel, 1991

zigzag one. However, an aggregation of diffusing particles has an observable drift, from places of higher concentration to places of lower concentration. For this reason diffusion is known as a transport phenomenon.

The average distance traveled by a molecule in the interval between collisions is known as the mean free path. It decreases with increasing concentration. Another quantity characterizing the diffusing substance is the displacement. By displacement is meant the

distance between the original position of a particle and its position after a certain period of time *t*. The mean displacement is zero, since in the absence of a difference in concentration, positive and negative displacement are equally probable. For this reason the mean square displacement is introduced.

The movement of gases in porous media such as soil occurs mainly by diffusion (Troeh, *et al.* 1982). The gas molecules move in response to a partial pressure or concentration gradient. Gaseous diffusion in soil occurs in the air-filled pore space between the solid particles and associated water films. It is the most important process causing gaseous interchange between the soil and atmosphere.

The diffusion coefficient measures the rate at which molecules spread out along a concentration gradient. It can be measured by observing the rate at which a boundary spreads or the rate at which a more concentrated solution diffuses into a less concentrated one (Atkins, 1986).

The diffusion coefficient depends on properties of the medium as well as those of the diffusing compound. It varies directly with the square of the absolute temperature and inversely with the total pressure (Baver *et al.*, 1972).

Gas transport through a soil is directly proportional to the diffusion coefficient, and to the gas concentration gradient. In predicting gas movement such as water vapor loss, the diffusion rate is combined with the continuity equation.

Penman studied the diffusion of gases through porous solids. He concluded that the rate of diffusion of a vapor through a porous body is less than that in free air because the cross-sectional area available for the movement of gaseous molecules is smaller and length of path the molecules must follow is longer because the passage way is tortuous

(Baver *et al.*, 1972). The rate of diffusion at steady state through a solid can be expressed by the equation:

$$\frac{dq}{dt} = \frac{D}{\beta} A \frac{\rho_1 - \rho_2}{l} \tag{3.11}$$

where A = the cross-sectional area of the solid,

l = length of the solid,

D = the diffusion coefficient,

β = a proportionality constant, and

ρ_1 and ρ_2 = partial pressures of the vapor on each side of length l of the solid

When the available cross-sectional area for diffusion and the effective path length the molecules must travel are taken into consideration, this equation becomes

$$\frac{dq}{dt} = \frac{D_0}{\beta} AS \frac{\rho_1 - \rho_2}{l_e} \tag{3.12}$$

where Do = diffusion coefficient in air,

S = pore space or porosity, and

l_e = effective path length through the solid.

From two equations above, it is seen that

$$D = D_0 S \frac{l}{l_e} \tag{3.13}$$

Soil particles reduce the effective cross-sectional area available to the fraction that is occupied by air. This is the same as the air-filled porosity, ε, the fraction of the volume that contains air. The particles also impede the transfer by changing the pathway for flow into a tortuous and poorly connected system of passage ways that reduces the flux by an impedance factor, *b*. If *D* is the diffusion coefficient for a gas diffusing through the soil, then

$$D / D_o = b\varepsilon \tag{3.14}$$

Penman adopted the constant 0.66 for *b* based on his own diffusion data. This value compares favorable with the inverse of Carman's value for tortuosity (Baver *et al.*, 1972).

Tortuosity due to the sinuous path of flow is the ratio of the effective length to apparent length of the path. The value is $\sqrt{2}$ for a 45° angle to the apparent direction of flow. The curve relating *D*/*D*o to *S* is shown in Figure 3.2. It is linear with a slope of 0.66 for sand.

Thibodeaux proposed a similar modification for the diffusion coefficient in porous media (1979). He indicated that the interfacial area through which the molecules move is reduced because it is partially filled with solids. The diffusivity is reduced because the diffusion distance along a tortuous path increase as shown in Figure 3.3.

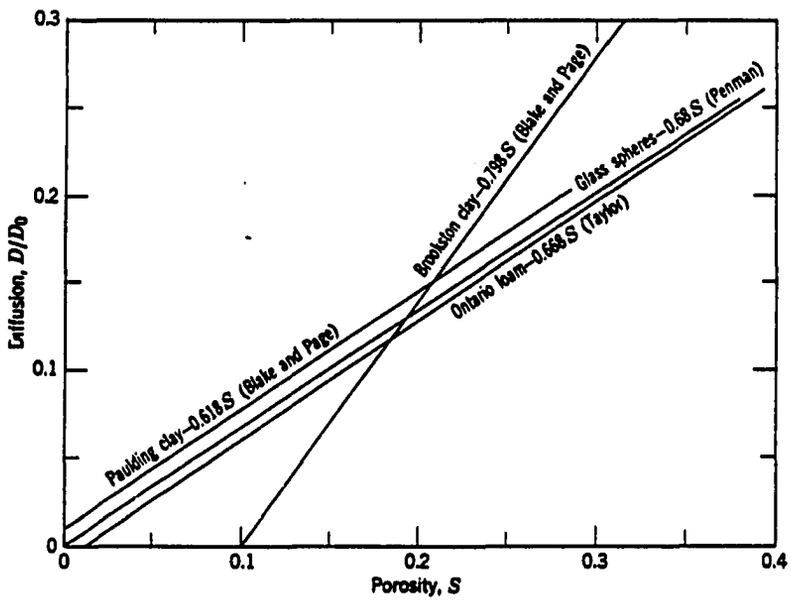


Figure 3.2. The relationship between diffusion ratio and porosity (Baver *et al.*, 1972)

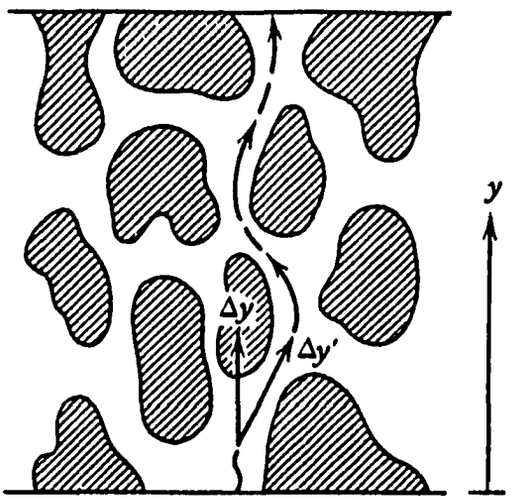


Figure 3.3. Pore diffusion in porous media (Thibodeaux, 1979)

The effective diffusion coefficient is formally defined as:

$$D = D_o \frac{\varepsilon}{\tau} \tag{3.15}$$

where D = the diffusion coefficient through the porous media,

Do = the diffusion coefficient in air,

ε = the porosity,

and τ = the tortuosity factor.

Total pore space is commonly greater in soils of fine texture than in those of coarse texture, so diffusion is potentially greater in dry soils of fine texture. However, moisture closes the fine pores of finely textured soils and this can reverse the expected diffusion behavior, making diffusion lower in soil of fine texture.

Table 3.3 lists several factors that influence diffusion and contaminant loss to the atmosphere (Pedersen and Curtis, 1991).

3.2.1 Fick's Laws

Robert Brown provided in 1827 the closest thing to direct, visual evidence for the motion of molecules. He observed that very minute particles suspended in a gas or liquid and viewed under a microscope were seen to be in a state of continual, random motion. Random molecular motion is sufficient to bring about diffusion.

Thomas Graham beginning in 1829 demonstrated that the relative rates at which gases diffuse is inversely proportional to the square roots of their respective densities or molecular weights (Thibodeaux, 1979).

In a paper published in 1855, Fick put Graham's experiments on a qualitative basis. The basic idea is that "the diffusion of the dissolved material... is left completely to the influence of the molecular forces basic to the same law... for the spreading of warmth in a conductor and which already been applied with great success to the spreading of electricity." In other words, diffusion has the same mathematical basis as Fourier's law of heat conductance or Ohm's law for electrical conduction.

Table 3.3. Variables affecting vapor transport and diffusion

Variables	Influence
Moisture content	Decreases effective porosity; vapor diffusion decreases strongly with increasing water content.
Adsorption	Adsorption decreases chemical concentration and therefore decreases vapor diffusion. Most volatile organic chemicals are non polar and adsorb primarily to organic matter.
Concentration	If not saturated, increasing concentration will increase vapor density and diffusion. The increase may be greater than proportional if the chemical vapor adsorption isotherm is nonlinear.
Temperature	Higher temperatures significantly increases vapor density for a given amount of chemical in soil, thereby increasing diffusion.
Solubility	The Henry's Law Constant (K_H) is an index of the partitioning between dissolved and gaseous phases. Compounds with large K_H values are more likely to move by vapor diffusion as opposed to liquid diffusion.

Reference: Pedersen and Curtis, 1991

The basic relationships governing diffusion can be understood using Fick's two laws (Hamaker, 1972). The first law can be visualized in terms of a fluid in a uniform tube with a unit cross-sectional area containing a dissolved material with a constant concentration gradient. This concentration gradient is attained by maintaining a constant concentration at one end (e.g., a saturated solution) and zero concentration at the other (Figure 3.4). Fick's first law says that the rate of transfer of material along this tube by diffusion will be directly proportional to the concentration gradient or rate of concentration change with respect to distance. This can be mathematically expressed as follows:

$$\text{Flux} = J = \frac{dq}{dt} = -D\left(\frac{\partial c}{\partial x}\right) \tag{3.16}$$

where $= \frac{dq}{dt}$ = the rate that material moves past a given point per unit cross-sectional area (g/cm^2-sec)

c = concentration (g/L)

x = the distance along the tube (cm)

D = diffusion coefficient (cm^2/sec)

(-) sign is essential because diffusion occurs in the opposite direction from the concentration gradient, i.e., from high to low concentration

The system shown in Figure 3.4 is operating under steady state conditions; that is, although diffusion is constantly transferring material from one end of the tube to the other, the concentration at any point along that tube remains constant and

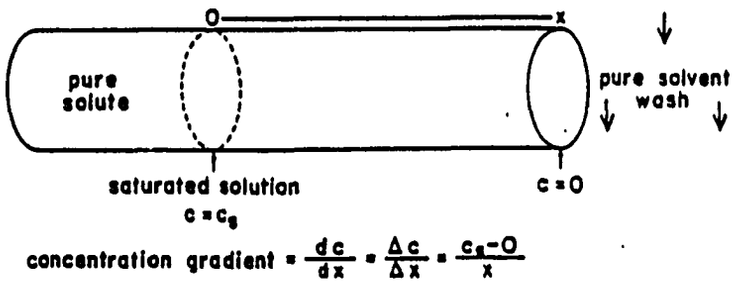


Figure 3.4. One dimensional case of steady-state illustrating Fick's first law of diffusion (Hamaker, 1972)

unchanging with time. Although the system is in constant dynamic flux, it appears to be static.

In many cases, however, systems are not operating under steady state conditions and it is impossible to apply Fick's first law. Fick's second law is a modification of first law obtained by applying the continuity equation to a differential element in the system. The rate of change in the concentration represents the difference between the rate of diffusion into and out of the element. This can be mathematically expressed as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{3.17}$$

Evaporation of gasoline and diesel fuels from soil is difficult to predict because of the many parameters affecting their adsorption, movement, and persistence. Gasoline and diesel fuels volatilize at a greatly reduced rate that depends not only on the equilibrium distribution between the air, water, and soil matrix as related to vapor pressure, solubility, and adsorption coefficients, but also on their rate of movement to the soil surface.

Call (1957) applied Fick's laws to diffusion in soil. He assumed the following factors when diffusion occurs in and through a porous medium.

1) Since diffusion takes place only through the air-spaces in the medium, the area available for diffusion will be much reduced. This area is assumed to be proportional to the porosity S of the medium.
2) Since the pores in the medium are tortuous, the distance traveled by a diffusing gas molecule is longer than the apparent path length. The dimension should, therefore, be multiplied by k, tortuosity factor.

The resulting diffusion equations are:

for steady state

$$J = -\frac{SDo}{k}\frac{\partial c}{\partial x} \tag{3.18}$$

for unsteady state

$$\frac{\partial c}{\partial t} = \frac{Do}{k}\frac{\partial^2 c}{\partial x^2} \tag{3.19}$$

where Do is the diffusion coefficient in free air.

3.2.2 Effect of Water Content of the Soil on the Volatilization

Volatilization is highly dependent upon the moisture content of the soil. Figure 3.5 shows the remaining concentration of TPH (Total Petroleum Hydrocarbons) in the soil with respect to moisture contents. The role of water content in the volatilization of organic chemicals is quite controversial (Pedersen and Curtis, 1991). Some researchers say that increasing water content increases the volatilization due to the displacement of organic chemicals with water; others say that increasing water content decreases volatilization due to the reduced pathway impeding the escape of organic chemicals from the soil.

Donaldson *et al.* (1992) studied the effects of water content on volatilization of gasoline compounds. They investigated the loss of 10 hydrocarbons which are found in gasoline (benzene, n-heptane, toluene, m-xylene, n-nonane, n-propylbenzene, 1,2,4-trimethylbenzene, n-butylbenzene, 1,2,4,5-tetramethylbenzene, and n-dodecane) from a 20-cm depth of soil in several field experiments. Soil was spiked with 50 mg/Kg of each compound, placed in pans outdoors, and subject to one of five treatments:

1) dry, unmixed soil
2) dry soil mixed weekly
3) soil watered once only
4) soil watered periodically
5) soil watered and mixed periodically

They found that significantly greater rates of loss occurred from wet soils, with an average of 5.7 percent remaining in wet and mixed treatments at the 18-20 cm depth on

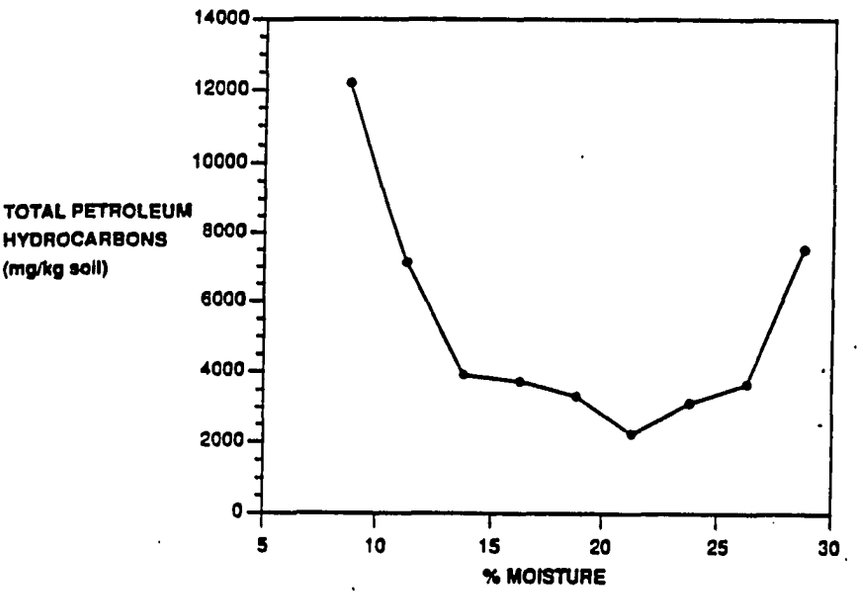


Figure 3.5. Total petroleum hydrocarbon content under various moisture contents (Frankenberger, 1992)

Day 32 of the experiment, compared with 61 percent remaining in dry, unmixed soils. They concluded that there was increase in desorption of the gasoline compounds from soil particles at higher moisture contents. The resulting increase in vapor pressure might have allowed diffusion to occur at an increased rate.

Water content affects volatilization losses by competing for adsorption sites on the soil (Thomas, 1982). For non-polar and weakly polar compounds, water is preferentially sorbed onto soil particles and can displace these compounds.

For weakly polar or nonionic compounds the fraction of soil organic matter is the most important soil factor in adsorption. Since most of the more volatile compounds are nonionic or only weakly polar, their adsorption by soil is closely related to organic matter content. Once the soil surfaces are saturated with a mono molecular layer of water, the vapor density of a weakly polar compound in the soil air is greatly increased, and additional soil water does not influence the tendency of the compound to leave its sorbed site.

The concept of "co-distillation" is that a compound is assumed to evaporate along with the soil moisture in the same ratio as they are present in the soil/soil-water system. Chemicals in the soil probably do not behave in this manner (Thomas, 1982). The loss of a compound in the presence of water is not due to co-distillation. When the water evaporates, the compound sorbs onto dry soil. Volatilization of the compound is enhanced by the presence of water, not its evaporation. Compound loss becomes insignificant when water loss decreases, because the vapor density is reduced by adsorption on the dry soil. Conversely, the presence of water causes desorption of the compound, increasing vapor density.

As a consequence of this behavior, a compound may be bound very strongly onto a dry soil, thereby reducing its volatilization rate. When soil is moistened, the water displaces the compound, allowing volatilization to occur at a faster rate. Keeping the soil dry will reduce or stop the volatilization of some chemicals, since the soil needs some moisture for the displacement or solubilization of the chemical. However, if the concentration of a compound in soil becomes so high that its chemical activity approaches that of the pure compound, the presence or absence of water will not affect its volatilization rate.

Researchers showed that the soil sorption coefficient is greater for drier soils. Sorption of contaminants to soil decreases as the water content increases and the contaminant molecules are displaced. Reible (Pedersen and Curtis, 1991) showed that electrostatic forces increase for drier soils, leading to reduced volatilization from the dissolved phase into the soil gas. Figure 3.6 shows schematically how soil moisture displaces volatile organic compounds (VOCs) and affects sorption.

On the other hand, some researchers indicate that an increase in moisture content in the soil decreases the volatilization of organic chemicals. Water content of the soil has competing effects on the air permeability. The primary effect of water is to reduce the air-filled pore space of a soil. Stephanatos concludes that the movement of soil gas is reduced as water content increases due to the physical reduction in available air pathways (Pedersen and Curtis, 1991).

Aurelius and Brown (1987) studied the volatilization flux of xylene spilled on the soil surface. Volatilization of xylene was measured using a chamber equipped with a granular activated carbon (GAC) vapor trap. They used three level of moisture content:

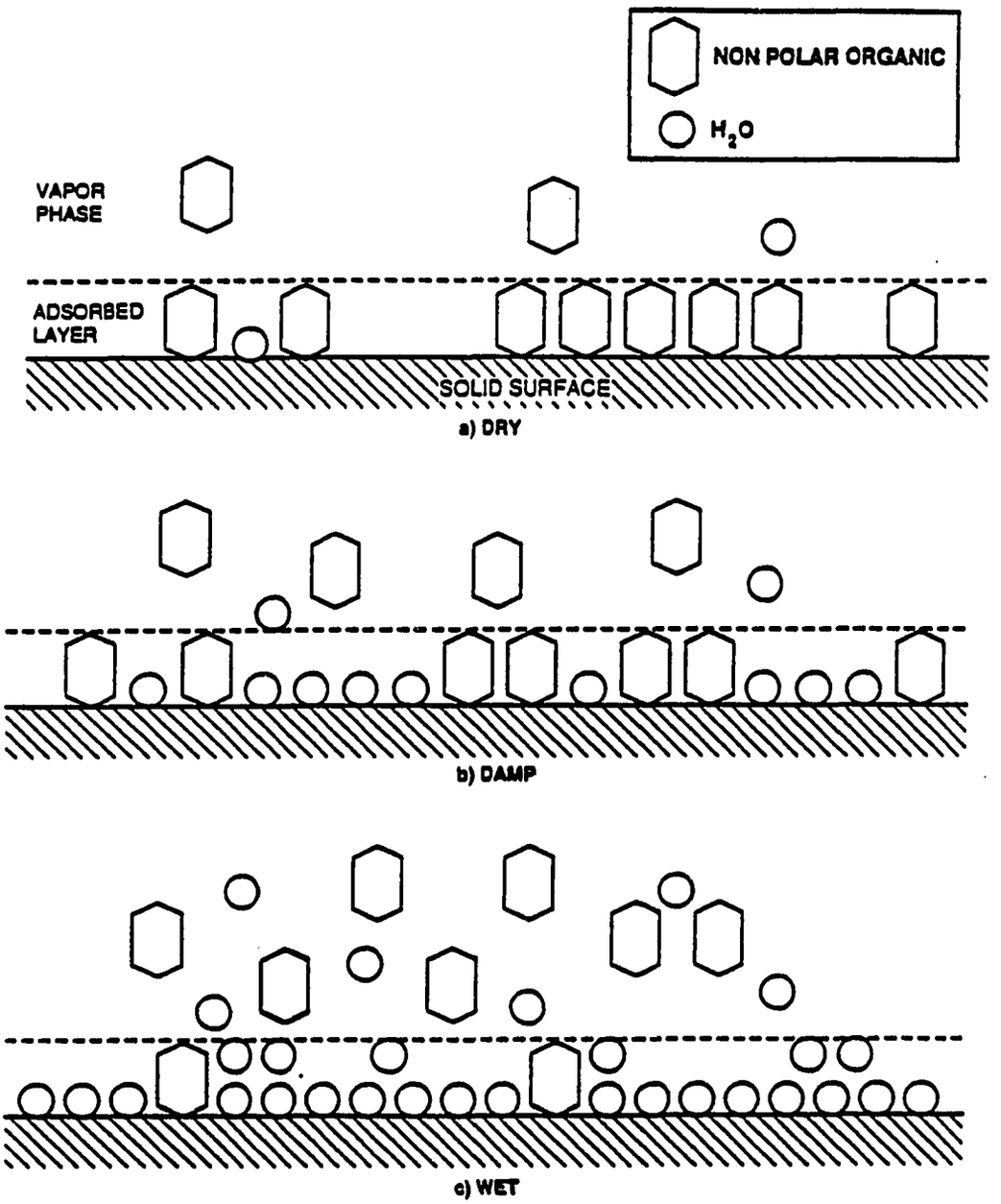


Figure 3.6. Illustration of VOC adsorption under three moisture contents (Pedersen and Curtis, 1991)

0.15, 0.2, and 0.26 kg of water per kg of dry soil. They found that most of the observed volatilization occurred immediately after spilling of xylene on the soil surface and was greatest from the driest soil. They concluded that an increase in soil moisture content would decrease volatilization due to a reduction in the air filled porosity.

Some researchers found that there is the optimum moisture content which results in the maximum amount of volatilization. Frankenberger (1992) showed that moist soils (18 percent g water/g soil) tend to show lower TPH (Total Petroleum Hydrocarbons) concentrations than drier and saturated soils (Figure 3.5).

The optimal soil moisture regime for maximum volatilization is a water content low enough to ensure the adequate air permeability yet wet enough to reduce electrostatic force. If the water content is low enough, organics will be tightly adsorb onto soil particles. If the water content is high enough, it can reduce the pore and slow down the loss of organics from the soil.

3.3 Volatilization in Bioremediation

The improper disposal, misuse, and accidental release of petroleum products such as gasoline and diesel oil into the environment has resulted in widespread pollution of soils, groundwater, and marine environments (Skladany and Metting, 1993). As the adverse environmental and health effects of these materials have become better known, increasing attention is being directed at the development and implementation of innovative technologies for cleaning up these kinds of contamination.

A variety of technologies are currently available to treat soils contaminated with fuels, including excavation and burial in a chemically secure landfill, vapor extraction, soil washing, soil flushing, critical fluid extraction, thermal desorption, and incineration. Some of these physicochemical treatment technologies do not actually destroy fuels. Rather, the chemicals are simply bound in a modified matrix or transferred from one phase or location to another (Thomas and Ward, 1989; Nelson *et al.*, 1990; Mahaffey *et al.*, 1992).

Bioremediation is an alternative that can destroy the fuels. It employs microorganisms to mediate desired chemical reactions or physical processes in transforming complex or simple chemical compounds into non hazardous forms (Thomas and Ward, 1989).

Several *in situ* bioremediation methods are shown schematically in Figure 3.7. Pump-and -treat extract and treat contaminated groundwater in the saturated zone. Percolation consists of applying water, containing nutrients and sometimes microorganisms to the contaminated soil surface and allowing it to penetrate into the soil. Bioventing supplies air to an unsaturated soil zone. Air sparging supplies air into the groundwater of a contaminated soil.

Ex situ bioremediation technology involves soil-treatment units, compost piles, and engineered biopiles (Figure 3.8). Oxygen and nutrients are supplied to each treatment technology. Soil-treatment units provide the soil with oxygen by tilling and apply water, nutrient, and possibly microbial inocula to the soil. Compost piles consists of soil supplemented with composting material such as wood chips, straw, manure, rice hulls to improve its water and air holding capacities. Compost piles require periodic mixing to provide oxygen to the soil. Engineered biopiles consist of soil that contain piping to provide air, water, and nutrients (Blackburn and Hafker, 1993).

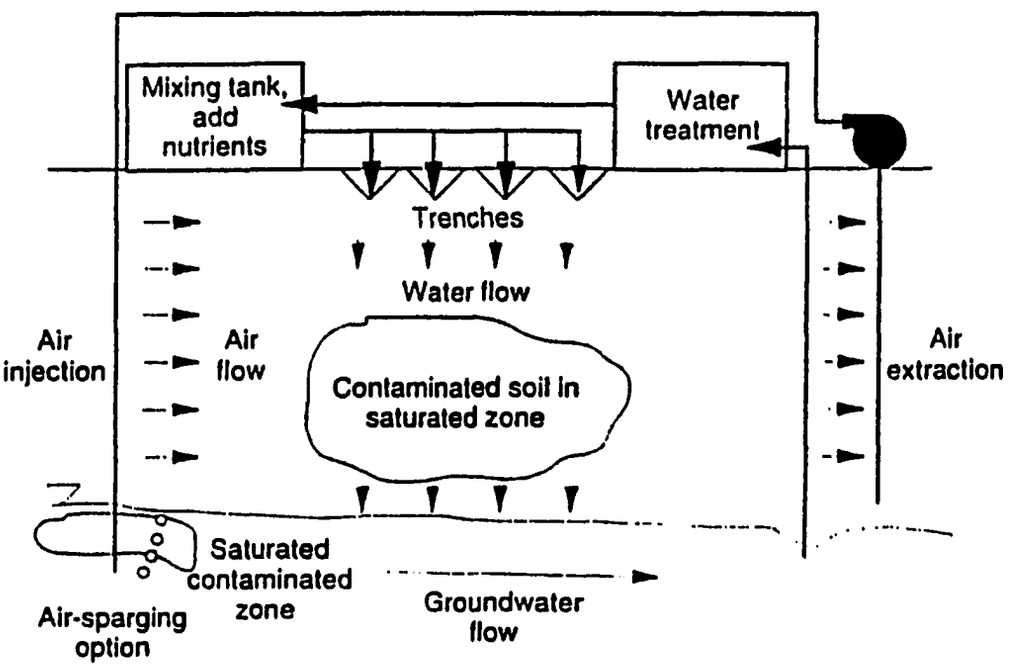


Figure 3.7. Flow diagram of *in situ* bioremediation technique (Blackburn and Hafker, 1993)

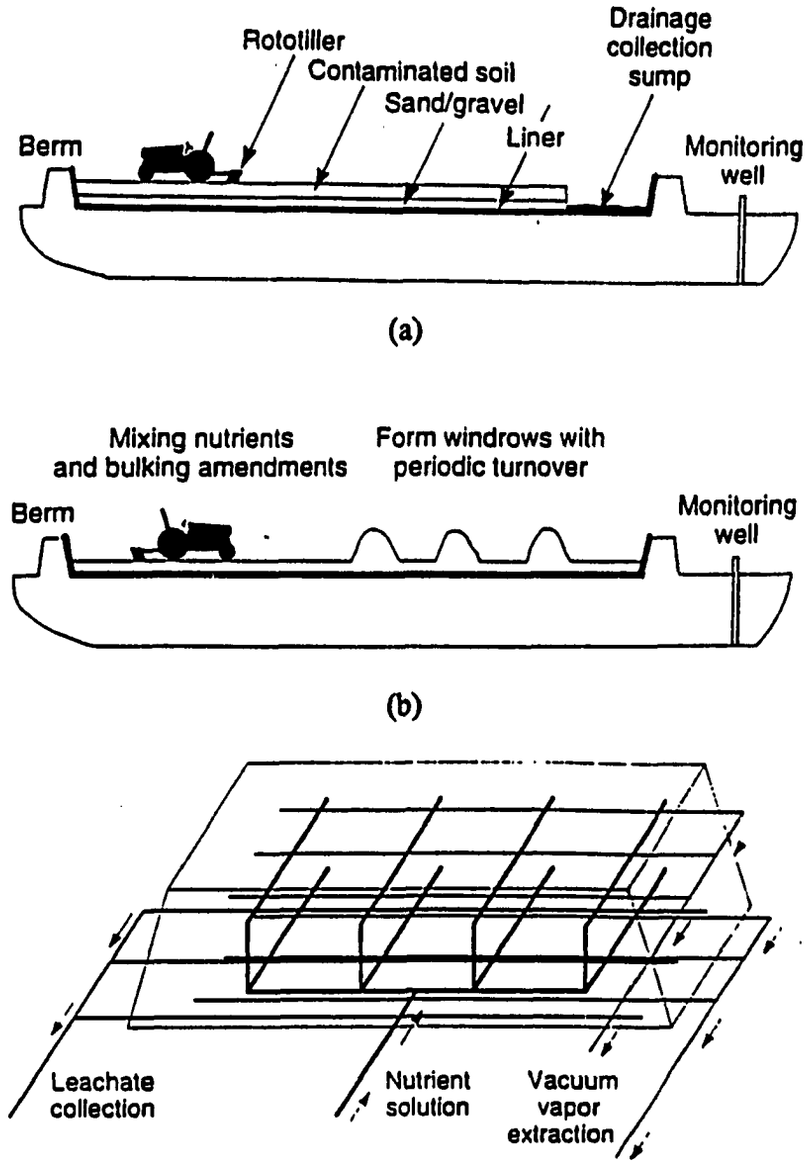


Figure 3.8. Various *ex situ* bioremediation techniques (Blackburn and Hafker, 1993): (a) Soil-treatment units, (b) Compost piles, and (c) engineered biopiles

Successful site remediation relies, however, on the proper utilization of microbial capabilities and a suitable growth environment made possible with appropriate engineering design (Skladany and Metting, 1993). The major advantage of bioremediation is that it is a natural process. Many organic compounds can be used as food by naturally occurring microorganisms in the soil (Hopper, 1989). Compounds that are considered hazardous can be transformed into innocuous products.

Although bioremediation has several important and distinct advantages for treating contaminated soils, it is not without its disadvantages. A major disadvantage of many biological processes is that they are often highly specific. Not all xenobiotic compounds are susceptible to rapid and complete biodegradation. Important site factors required for success include the presence of metabolically capable microbial populations, suitable environmental growth conditions, acceptable soil composition and properties, and appropriate concentrations of substrates and nutrients (Fredrickson *et al.*, 1993).

Also, biodegradation end products other than CO_2 and H_2O can be equally or more persistent or hazardous than the initial parent compounds. For example, depending on site condition, biotransformation of the chlorinated aliphatic trichloroethylene (TCE) can result in the formation and accumulation of vinyl chloride, a suspected carcinogen (Nelson *et al.*, 1987; Little *et al.*, 1988).

Jamison *et al.* (1975) carried out bioremediation tests on water contaminated by leakage from gasoline pipeline. They found that nitrogen, phosphate, and oxygen are limiting factors for microorganisms to utilize gasoline as the sole carbon source. By adding fertilizer and air to contaminated soils in the field, they confirmed their laboratory results.

Song *et al.* (1990) evaluated the effectiveness of bioremediation treatment in cleaning up various type of soil which were separately contaminated at 50 to 135 mg/g of

soil by five types of fuel including gasoline and diesel fuels. Experimental variables included contamination level, incubation temperature, and soil type. Contamination levels consisted of 50, 100, and 135 mg fuel/g of soil. Incubation temperatures were 17, 27, and 37°C. Soil type included sand, loam, and clay loam. Three treatments were compared; no treatment, bioremediation treatment, and poisoned evaporation controls. Bioremediation treatment included liming to raise the pH to 7.5-7.6, fertilizing, and weekly tilling. Indigenous microorganisms were used for bioremediation without identification.

They found that the optimum temperature was 27°C and that the initial fuel concentrations did not play an important role in their experiment. They also found that sand was least favorable soil type for bioremediation due to its poor absorbing capacity and low microbial diversity. Biodegradation played a smaller relative role in the removal of gasoline hydrocarbons from soil than it did with other fuels. The C_6 to C_9 components of gasoline, under their experiments, were lost more rapidly by evaporation than by biodegradation, while biodegradation was more effective for the C_{10}-C_{11} components. Bioremediation reduced the diesel half-life by 50 percent or more.

Wang and Bartha (1990) conducted bioremediation tests with soils contaminated with three kinds of fuel oil (jet fuel, heating oil, and diesel oil), respectively. One of each set of triplicates was left untreated, one was only tilled weekly, and the other received complete bioremediation treatment consisting of liming, fertilization and weekly tilling. Liming increased the pH from 6.7 to 7.4. Fertilization produced carbon to nitrogen and carbon to phosphorus ratios of 200:1 and 1000:1, respectively. By conducting parallel hydrocarbon residue and microbial activity measurements, they confirmed that biodegradation was the dominant component of the remediation process.

Song and Bartha (1990) studied the effects of jet fuel spills on the microbial community of soil. They measured the hydrocarbon residues, microbial numbers, and microbial activity in loam soil contaminated with jet fuel resulting in 50 and 135 mg of hydrocarbon per g of soil. Contaminated soil was incubated at 27°C either as well-aerated surface soil or as poorly aerated subsurface soil. Hydrocarbon residues were measured by gas chromatography. Measurements included direct counts of bacteria, mycelial length, plate counts of aerobic heterotrophs, and most probable numbers of bacteria. Activity was determined by fluorescein diacetate (FDA) hydrolysis.

In their study jet fuel disappeared about twice as fast from surface soil as it did from subsurface soil. They concluded that the increased rates of jet fuel could not be ascribed to evaporative losses alone but were caused, in roughly equal proportions, by higher evaporation and the faster biodegradation rates as a result of the increased oxygen availability in surface soil.

4. EXPERIMENTAL DESIGN

Work in progress at Iowa State University has employed two products as *ex situ* bioremediation agents for soil contaminated with petroleum products. Both of these agents appear to be effective in stimulating growth of microorganisms in contaminated soil. One of the agents is a natural product (soy hulls), and the other is a proprietary material (a modified natural product) derived from crop residues.

One of the benefits that these agents might provide in bioremediation is a wicking or emulsifying action that would hold the petroleum product in the contaminated zone and prevent leaching to greater depths and possible loss by evaporation. The goal of this study was to determine what part of the removal of petroleum products being observed was due to biological activity and what part was due to evaporation. It was also intended to develop the mathematical model to predict the fate of petroleum products in contaminated soil. For these purpose the following experiments were conducted:

1) The movement of petroleum products in contaminated soil,
2) The effect of particle size of the sand on the volatilization of petroleum products in contaminated soil.
3) The effect of initial concentration of petroleum products on the volatilization in contaminated soil,
4) The effect of moisture content on the volatilization of petroleum products in contaminated soil, and
5) The effect of organic matter on the volatilization of petroleum products in contaminated soil.

6) The interaction between water, petroleum products, and sand particle, and

4.1 Materials and Apparatus

Commercial unleaded gasoline and #2 diesel fuel were used in the study. These materials were obtained from a local service station. The density of gasoline was 0.75 g/ml and that of diesel fuel was 0.9 g/ml. The soy hulls were obtained from Cargill Soy Processing Plant in Iowa Falls, Iowa. The moisture content of soy hulls was about 10 percent based on the dry weight of soy hulls. The MNP was obtained from the manufacturer, an Iowa based company. Further information about MNP was not available because it was not permitted from the manufacturer. The moisture content of MNP was about 20 percent based on the dry weight of MNP. Volatilization of petroleum products was determined gravimetrically using a digital balance which had a maximum capacity of 200 g ± 0.01 g (MB 200, Ohaus Company).

4.2 Sand Properties

Two sizes of sand were used to observe the effect of particle size in the volatilization tests. A coarse and a fine sand were prepared by sieving sand obtained from Hallett construction pit which is located about 5 miles north of Ames. From the result of quantitative X-ray diffraction, it was found that the sand contains 62.5 percent quartz,

18.4 percent dolomite, 10.3 percent feldspar, 5.3 percent limestone, and 0.5 percent clay. The particle size of the coarse sand ranged from 0.84 to 2.0 mm (#10 to #20 mesh). The particle size of the fine sand ranged from 0.25 to 0.84 mm (#20 to #60 mesh). The average particle size of the coarser sand was 1.42 mm and that of finer sand was 0.55 mm. Both the coarse and the fine sand were washed with distilled water to remove subsieve materials. The particle density, bulk density, and porosity were the same for both the coarse and the fine sand:

particle density = 2.65 g/ml
bulk density = 1.85 g/ml
porosity = 0.40

4.3 Volatilization Test Procedure

About 190 g of dried clean sand was weighed, transferred into a flask. The weight used (190 g) was kept close to the capacity of the balance to minimize errors in measuring residual petroleum in the soil. The flask was stoppered with a silicone stopper to minimize the volatilization of petroleum products. The stopper was tightly wrapped with aluminum foil to prevent a reaction of petroleum product with the silicone. Pre-calculated amounts of water and petroleum products were poured into the flask. The contents of the flask were shaken by hand for about 10-15 minutes to make a homogeneous mixture of sand and petroleum products. The mixture was transferred into weighing vessels (a 25 ml plastic graduated cylinder, a 100 ml plastic graduated cylinder, or an aluminum foil dish)

and placed in a hood. Changes in weight were monitored semi-continuously. Some fuel probably was adsorbed by the plastic cylinder but the amount was considered negligible so no correction was made for that. This might cause an experimental flaw; therefore, plastic cylinder should not be used for future work. The aluminum dishes were obtained from a local grocery store. The shape and dimensions are shown in Figure 4.1. The diameters and surface areas of the three types of weighing vessels used are shown in Table 4.1.

A cross-section through the hood is shown in Figure 4.2. The dimension of hood was 100 cm wide, 65 cm deep, and 120 cm high. The vapor is quickly swept away by the air flow (Figure 4.2). Air flow enters an opening produced by blocking off the

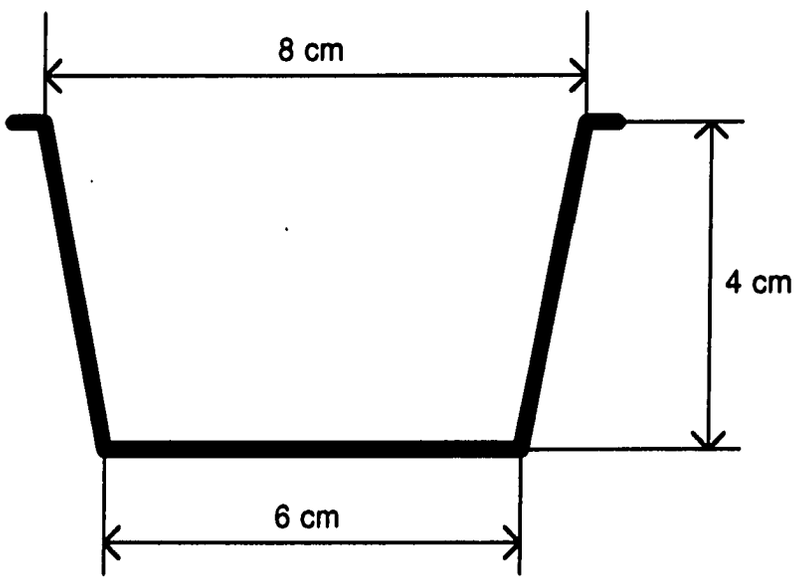


Figure 4.1. The shape and dimensions of aluminum dish

Table 4.1. Diameters and surface areas of three types of weighing vessels

Dish Type	Diameter (cm)	Surface area (cm^2)
25 ml graduated cylinder	1.8	2.54
100 ml graduated cylinder	2.7	5.73
Aluminum dish	7.0*	38.48*

* Average value based on top and bottom of aluminum dish

lower part of the space under the door. The height of the top surface of the contaminated soil sample was elevated to the bottom of the opening to create a draft over the surface. When the height of the opening was 0.41 cm (area = 0.41 m^2), the air flow was 18.75 m^3/min or a velocity of 0.76 m/sec. During the volatilization test, the height of the opening was reduced to 3 cm. Thus, the velocity is so high that all vapor will be swept away.

4.4 Movement of Gasoline in Sand Mixture

One of the purposes of the study was to determine how petroleum products move through the contaminated sand and escape into the atmosphere as a vapor. Two types of tests were conducted to study the movement of gasoline in sand. The first test was used to

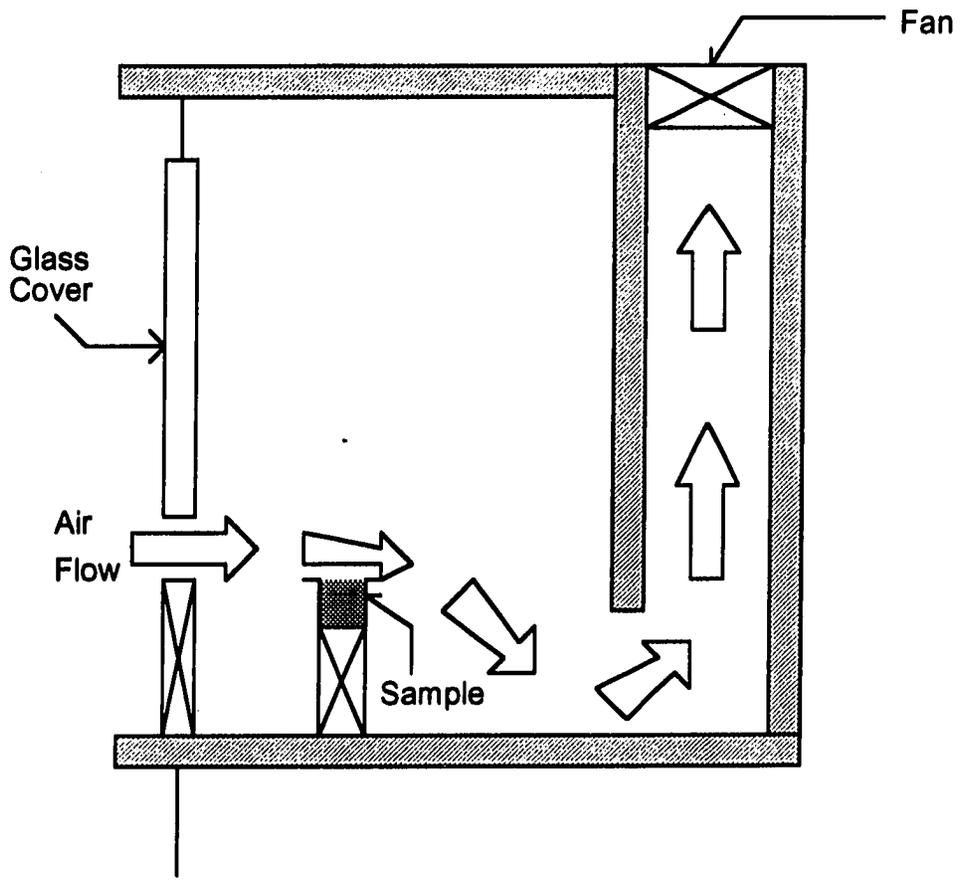


Figure 4.2. Side view of the hood

measure the concentrations of gasoline at various times and depths. The second test was used to compare the volatilization fluxes of gasoline when dry sand was placed on top of the sand fuel mixture. This was intended to model the way that volatilization would change as the level of the free product zone receded.

In the first test, some measurements were made at 1, 2, and 3 days (long time period) and others were made at 1, 5, and 12 hours (short time period) after sample was prepared. The containers used in these tests were 60 ml Nalgene syringes. The delivery end of the syringe was cut off to produce a graduated cylinder with a movable bottom (Figure 4.3). Some fuel probably was adsorbed by the plastic syringe wall but the amount was considered negligible so no correction was made for that. This might cause an experimental flaw; therefore, plastic syringe should not be used for future work. Since bottom part (50-60 ml) contacts the rubber tip of the plunger which could react significantly with fuel, the concentration in the bottom 10 ml was not measured.

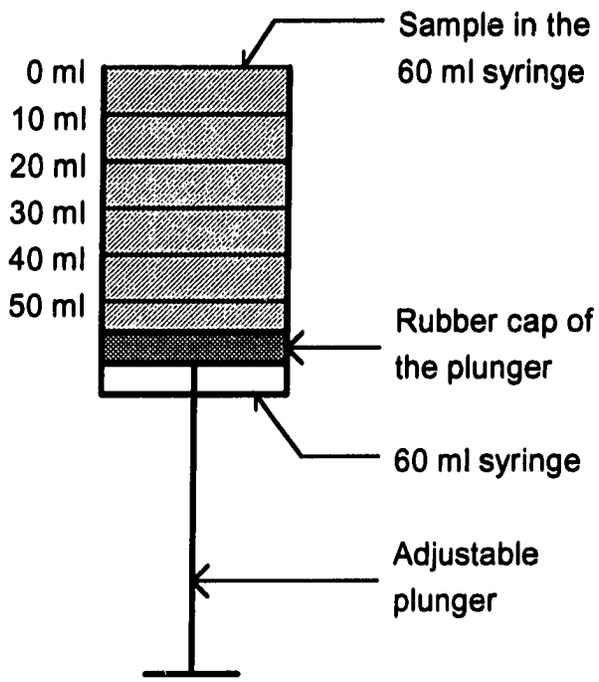


Figure 4.3. Diagram of test syringe

The target value for the initial concentration of gasoline in sand was about 0.05 g gasoline/g dry sand. This is lower than the amount of gasoline that will cling to the sand after being saturated and drained. That amount was found to be 0.1 g gasoline/g dry sand.

The sand and gasoline mixture was mixed in a flask by shaking by hand for about 10 to 15 minutes. The actual value for the initial gasoline concentration that was obtained was about 0.04 g fuel/g dry sand. About 20 percent was lost by volatilization during mixing and pouring sand into each syringe. The sand gasoline mixtures were compacted using the plungers to obtain nearly the identical starting conditions. After compacting the wet samples in the syringes, the syringes were placed in the hood. A total of 12 syringes were used for this experiments; 6 for the longer time periods (1, 2, and 3 days) and 6 for the shorter time periods (1, 5, and 12 hours). Duplicate samples were removed from hood at each measuring time. One sample from each duplicate was taken from the early part of sample preparation and the other duplicate was taken from the latter part to eliminate the effects of volatilization while making samples. Aliquots consisting of 10 ml of wet sand were expelled using the syringe's plunger. The aliquots of wet sand was weighed and placed in a oven for 1 day to measure liquid content in the wet sample. Based on these measurements, the concentrations of gasoline at each sampling time were determined. The top sand poured easily because it's fuel was already mostly gone. Sand at lower depths in the syringe contained more fuel and was more cohesive so a knife was used to strike off the aliquot.

The second test was used to determine the volatilization flux of gasoline when dry sand was placed on top of the sand fuel mixture. This was intended to model the way that volatilization would change as the zone containing free product was receded from the surface. For this experiment, seven Nalgene 100 ml graduated cylinders containing varying

amounts of sand containing gasoline and a cap of dry sand were used (Figure 4.4). The top of each graduated cylinders was cut off at the 100 ml mark (the level of the sand surface) to provide good exposure of the sand surface to the flow of air. The target value for the initial concentration of gasoline in the sand was about 0.05 g gasoline /g dry sand.

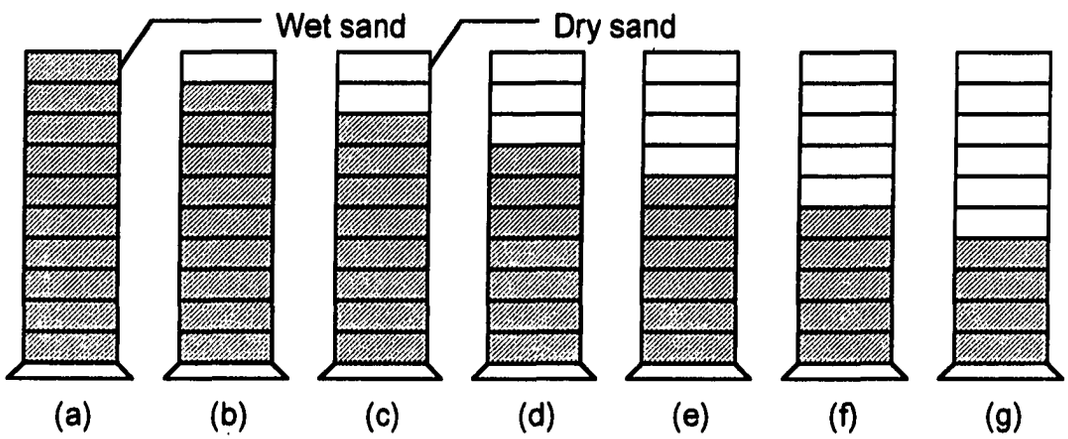


Figure 4.4. The diagram of system for comparison of volatilization fluxes (a) 100 ml gasoline-contaminated sand, (b) 90 ml gasoline-contaminated sand capped with 10 ml dry sand, (c) 80 ml gasoline-contaminated sand capped with 20 ml dry sand, (d) 70 ml gasoline-contaminated sand capped with 30 ml dry sand, (e) 60 ml gasoline-contaminated sand capped with 40 ml dry sand, (f) 50 ml gasoline-contaminated sand capped with 50 ml dry sand, (g) 40 ml gasoline-contaminated sand capped with 60 ml dry sand

4.5 The Effect of Particle Size on the Volatilization

The purpose of this test was to determine whether the rate of volatilization was different for the coarse and the fine sand. Two kinds of tests were conducted. The first kind of test was used to measure the loss of gasoline from a homogenous mixture of sand and gasoline. The second kind of test was used to measure the loss of fuel through dry sand. The test employing dry sand was done by pouring dry sand over a pool of gasoline in an aluminum foil dish. In both kinds of tests, the loss of weight was measured at various times and used to calculate the rate of volatilization of the gasoline.

4.6 The Effect of Initial Concentration of Petroleum Products on the Volatilization

The purpose of these tests was to determine the relationship between the initial concentration and the rate of volatilization. For these tests, the initial concentrations investigated ranged from 0.003 to 0.09 g of gasoline/g of dry sand. Aluminum dishes and 25 ml graduated cylinders were used as weighing vessels in these experiments.

4.7 The Effect of Moisture Content on the Volatilization

Several tests were done to measure the effects of moisture content on the volatilization of petroleum products. Three different moisture contents were used; 5, 10,

and 15 percent which were based on the weight of dry sand. A fuel content of 3 percent was used. A higher fuel content might have resulted in drainage losses at higher moisture contents and a lower fuel content would have increased the error in measuring the loss of fuel due to volatilization. Aluminum dishes were used as weighing vessels. The sand/fuel/water mixtures used are shown in Table 4.2.

4.8 The Effects of Organic Matter on the Volatilization

Tests were run to determine whether organic matter would affect the volatilization of gasoline. The gasoline content used was 3 percent. Two types of organic matter

Table 4.2. Sand/fuel/water mixture used in studying effects of moisture content on volatilization

Sample #	Sample	Preparation
1	3 % Fuel	250 g Dry sand + 7.5 g Fuel
2	5 % Water	250 g Dry sand + 12.5 g Water
3	10 % Water	250 g Dry sand + 25.0 g Water
4	15 % Water	250 g Dry sand + 37.5 g Water
5	3 % Fuel + 5 % Water	250 g Dry sand + 7.5 g Fuel + 12.5 g Water
6	3 % Fuel + 10 % Water	250 g Dry sand + 7.5 g Fuel + 25.0 g Water
7	3 % Fuel + 15 % Water	250 g Dry sand + 7.5 g Fuel + 37. 5 g Water

(bioremediation agents) were used in these tests. One was a modified natural product (MNP) and the other was soy hulls. In order to investigate the effect of the MNP, three levels were used; 0, 10, and 40 percent of the total volume of the MNP and sand. The bulk density of the MNP is about 0.25 g/ml. The moisture content of the MNP was about 20 percent based on dry weight of MNP. The preparations were made by weighing out the quantities of the MNP and sand needed to obtain the desired volume percentages. The sample preparations used are shown in Table 4.3.

Table 4.3. The preparation of samples to study the effect of MNP on volatilization of gasoline

Sample Name	Preparation
0 % MNP	250 g Dry sand + 7.5 g Gasoline
10 % MNP	250 g Dry sand + 4.08 g MNP + 7.5 g Gasoline
40 % MNP	250 g Dry sand + 24.5 g MNP + 7.5 g Gasoline

Tests were also run to determine whether soy hulls would affect the volatilization of gasoline. The gasoline content used was 3 percent. Two levels of soy hull were added; 0, and 40 percent of the total volume of soy hulls and sand. The moisture content of soy hulls was about 10 percent based on dry weight of soy hulls. Duplicates were used. The bulk density of the soy hulls is about 0.1 g/ml. The sample preparations used are shown in Table 4.4.

Table 4.4. The preparation of samples to study the effect of soy hulls on volatilization of gasoline

Sample Name	Preparation
0 % Soy hulls	250 g Dry sand + 7.5 g Gasoline
40 % Soy hulls	250 g Dry sand + 7.5 g Soy hulls +7.5 g Gasoline

In order to more investigate the effects of organic matter on the volatilization of fuel, another tests were conducted. In these tests, sand was not used. The preparations used in studying the effects of MNP on the volatilization of petroleum products are shown in Table 4.5. The preparations for the effect of soy hulls on the volatilization of petroleum productsare shown in Table 4.6.

4.9 Interactions between Water, Petroleum Products, and Sand Particles

Two sets of experiments were conducted to study interactions between water, gasoline, and sand particles. The purpose of these experiments was to see if water would displace gasoline from the sand and whether gasoline would displace water from the sand. Literature search indicated that either result is possible.

Table 4.5. The preparation of samples used in studying the effects of MNP on the volatilization of petroleum products without sand

Sample #	Sample Name	Preparation
1	MNP-W	15 g MNP + 7.5 g Water
2	MNP-G	15 g MNP + 7.5 g Gasoline
3	MNP-D	15 g MNP + 7.5 g Diesel
4	MNP-GW	15 g MNP + 7.5 g Gasoline + 7.5 g Water
5	MNP-DW	15 g MNP + 7.5 g Diesel + 7.5 g Water

"MNP-W" stands for the mixture of MNP and water;
"MNP-G" stands for the mixture of MNP and gasoline;
"MNP-D" stands for the mixture of MNP and diesel;
"MNP-GW" stands for the mixture of MNP, gasoline, and water; and
"MNP-DW" stands for the mixture of MNP, diesel, and water.

- Displacement with water:

One-hundred-grams of clean, dry sand was poured into a 250 ml Erlenmeyer flask and 3 ml of gasoline was added. The contents of the flask were mixed by shaking by hand for 30 minutes. The gasoline completely coated the sand particle during this process. Then 100 ml of distilled water was added to the flask submerging the sand mixture. After 1 day, the supernatant was decanted into a 100 ml graduated cylinder and the volume of liquid was recorded.

Table 4.6. The preparation of samples used in studying the effects of soy hulls on the volatilization of petroleum products without sand

Sample #	Sample Name	Preparation
1	Soy-W	10 g Soy hulls + 5 g Water
2	Soy-G	10 g Soy hulls + 5 g Gasoline
3	Soy-D	10 g Soy hulls + 5 g Diesel
4	Soy-GW	10 g Soy hulls + 5 g Gasoline + 5 g Water
5	Soy-DW	10 g Soy hulls + 5 g Diesel + 5 g Water

"Soy-W" stands for the mixture of soy hulls and water;
"Soy-G" stands for the mixture of soy hulls and gasoline;
"Soy-D" stands for the mixture of soy hulls and diesel;
"Soy-GW" stands for the mixture of soy hulls, gasoline, and water; and
"Soy-DW" stands for the mixture of soy hulls, diesel, and water.

- Displacement with gasoline:

One-hundred-grams of clean, dry sand was poured into a 250 ml Erlenmeyer flask and 3 ml of distilled water was added. The contents of the flask were mixed by shaking for 30 minutes. The water completely coated the sand particle during this process. Then 100 ml of gasoline was added to the flask submerging the sand mixture. After 1 day, the supernatant was decanted into a 100 ml graduated cylinder and the volume of the liquid was recorded.

5. RESULTS AND DISCUSSION

5.1 Movement of Gasoline in Sand Mixture

Figure 5.1 shows how the gasoline concentration varied with depth. The average concentration values for a 10 ml volume element have been plotted at the mean depth value for each volume element. These results demonstrate that the gasoline concentration dropped rapidly near the surface. The concentration at greater depths receded more slowly. After several days, the concentration was nearly uniform throughout the sand, however. In characterizing the way that concentration was changing, the sand appeared to be drying out from the top down.

To test this hypothesis, a second set of experiments was performed by comparing the fluxes from contaminated sand capped with different amounts of dry sand. In this experiment, 100 ml graduated cylinders were used as weighing vessels. Again, no corrections were made for fuel adsorbed by the plastic cylinders. Figure 5.2 showed the amounts of gasoline volatilized.

The "100+0" in the legend stands for 100 ml of sand contaminated with gasoline with no cap of dry sand. The "90+10" has 90 ml of sand contaminated with gasoline capped with 10 ml of dry sand, etc. Initial fluxes (the amount of gasoline removed divided by surface area and time segment) for each composition were calculated except for the "100+0" sample. For the "100+0" sample, all fluxes according to time were calculated and were used for comparison with individual fluxed obtained from the others.

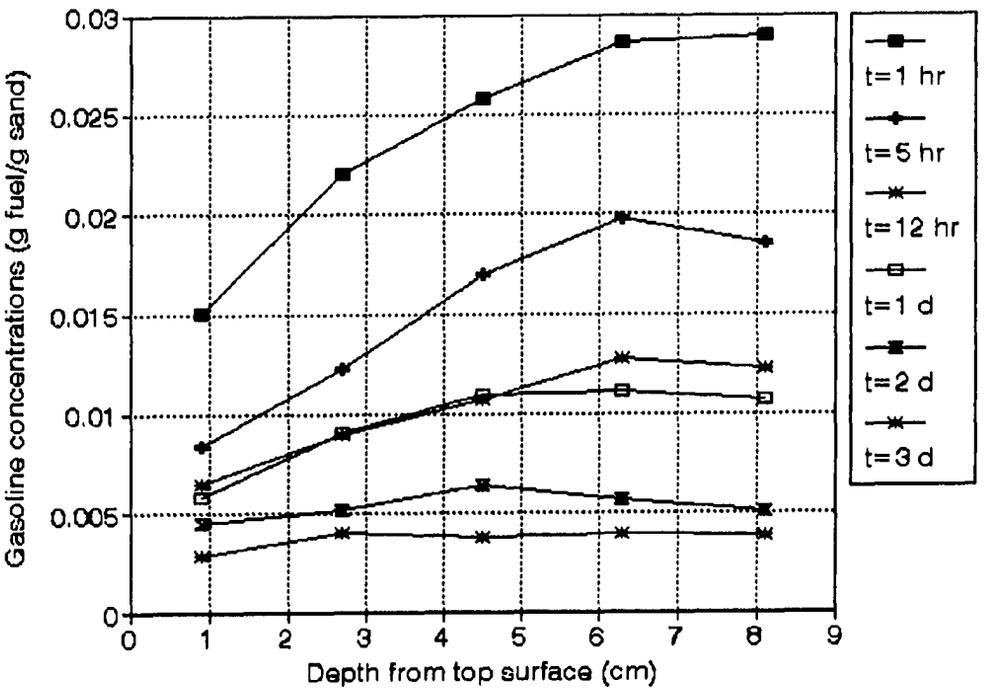


Figure 5.1. Movement of gasoline in sand; duplicate samples; initial concentration of gasoline = 0.05 g gasoline/g dry sand

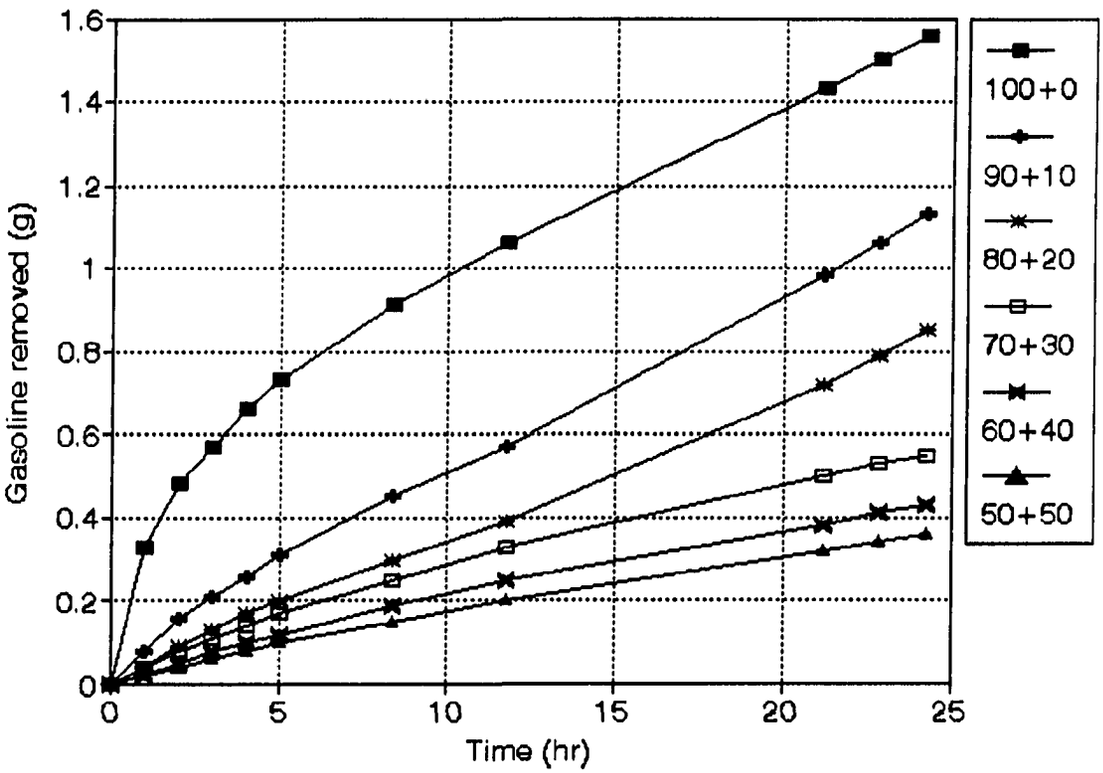


Figure 5.2. The amount of gasoline volatilized under various composition with dry sand; single data for each set; "100+0" for 100 ml gasoline-contaminated soil; "90+10" for 90 ml gasoline-contaminated soil capped with 100 ml dry sand; "80+20" for 80 ml gasoline-contaminated soil capped with 20 ml dry sand; "70+30" for 70 ml gasoline-contaminated soil capped with 30 ml dry sand; "60+40" for 60 ml gasoline-contaminated soil capped with 40 ml dry sand; "50+50" for 50 ml gasoline-contaminated soil capped with 50 ml dry sand

If we assume that "100+0" is drying out from the top down, corresponding times can be calculated from individually obtained initial fluxes of each composition and initial gasoline amount using the graph showing the amount of gasoline removed of sample "100+0". The total gasoline amount in "100+0" was 6.8 g. The calculations are shown in Table 5.1.

As an example, for the "90+10" sample the initial amount would be 0.9 of 6.8 or 6.12 g because only 90 ml contains gasoline and the 10 ml cap does not contain gasoline. Therefore, the initial difference amount between "100+0" sample and "90+10" sample would be 6.8 minus 6.12 or 0.68 g. From Figure 5.2 for "100+0" sample, time at which the removed amount of gasoline reaches 0.68 g is about 4 hr or 240 min. This is denoted as "Removal time (min)" in Table 5.1.

Therefore, as the level of gasoline free product in the sand recedes during volatilization, 10 ml sand will be dried and remaining 90 ml sand will contain 6.12 g of gasoline after 240 min. The volatilization flux of "100+0" at that time is about 0.85 g gasoline/cm^2/day which is calculated from Figure 5.2. Figure 5.3 shows the volatilization fluxes of "100+0" (□). The initial volatilization flux of "90+10" was 0.840 g gasoline/cm^2/day. This implies that the flux from "100+0" when upper 10 ml sand is dried is the same to the initial flux of "90+10" which is the mixture of 90 ml wet sand capped with 10 ml dry sand.

Initial fluxes for the removal time were plotted in Figure 5.3 and compared with the corresponding flux of "100+0". The fluxes for various compositions compared reasonably to those for "100+0". The assumption that the sand was drying out from the top down appears to be confirmed. If this assumption was not true, the fluxes for various

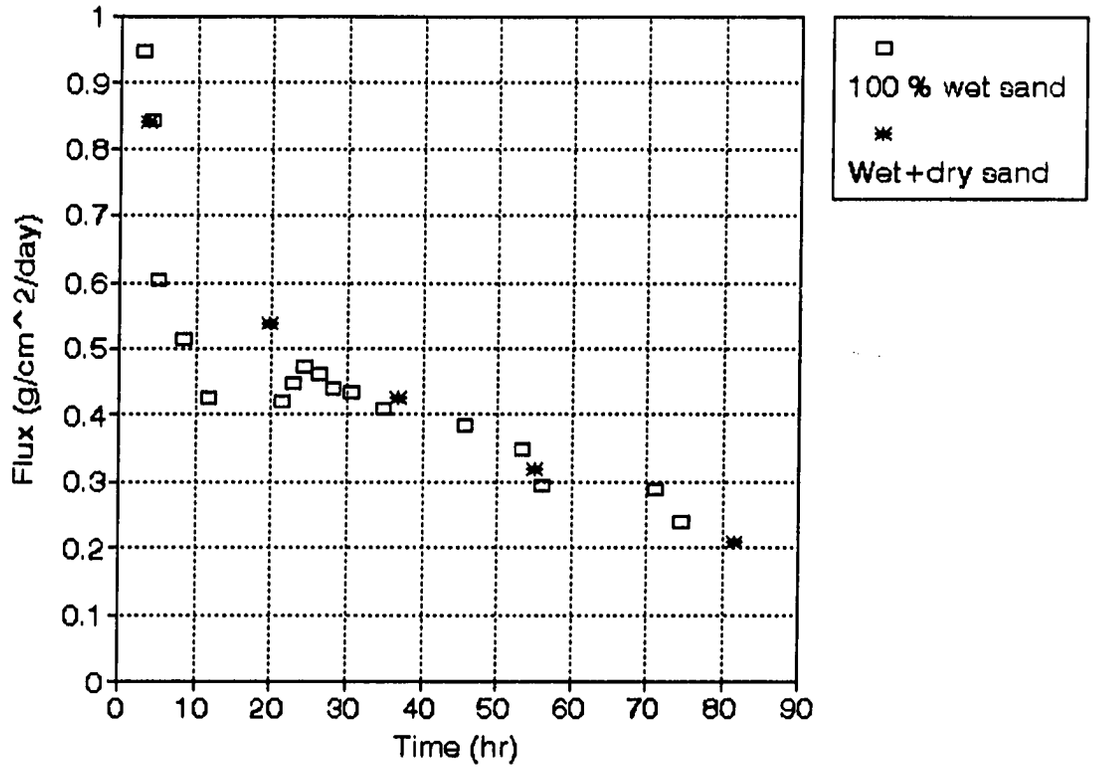


Figure 5.3. The comparison of fluxes; individual fluxes vs. fluxes from 100 ml wet sand; singe data; "100 % wet sand" represents the fluxes from 100 ml gasoline-contaminated sand; "wet+dry sand" represents fluxes from the gasoline-contaminated sand capped with dry sand from each composition such as 90 ml gasoline-contaminated sand capped with 10 ml dry sand

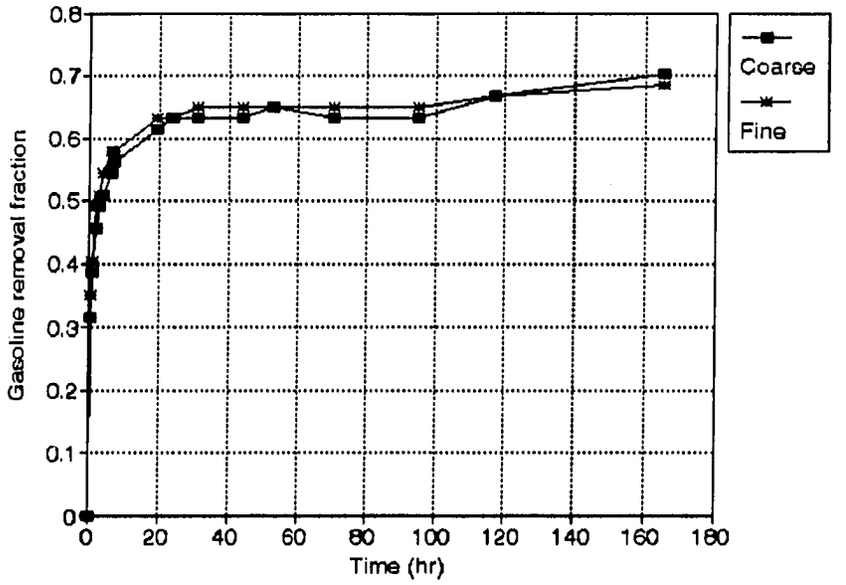
compositions (* from Figure 5.3) would not coincide with the fluxes graph of "100+0" sample. Instead, they would be scattered.

5.2 The Effect of Particle Size on the Volatilization

The effect of particle size on the volatilization of gasoline was investigated at three different concentrations. Tests were conducted using aluminum dishes. Figure 5.4 (a) shows the fraction of the total gasoline removed by volatilization for the coarse and the fine sand at an initial gasoline concentration of 0.003 g gasoline/g dry sand. C and F in the legend stand for coarser and finer sand, respectively. Figure 5.4 (b) and 5.4 (c) show fraction removed for initial gasoline concentrations of 0.007 g gasoline/g dry sand and

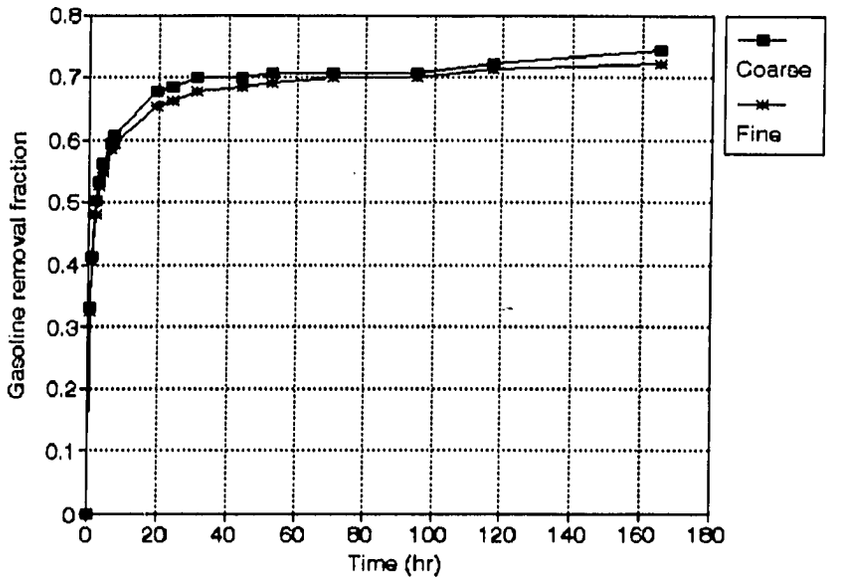
Table 5.1. Calculation of individual gasoline fluxes' corresponding time to the flux of 100 ml graduated cylinder

Sample number	Initial flux ($g/cm^2/d$)	Initial amount (g)	Removed amount (g)	Removal time (min)
"90+10"	0.840	6.12	0.68	240
"80+20"	0.537	5.44	1.36	1180
"70+30"	0.423	4.76	2.04	2200
"60+40"	0.316	4.08	2.72	3300
"50+50"	0.208	3.40	3.40	4900

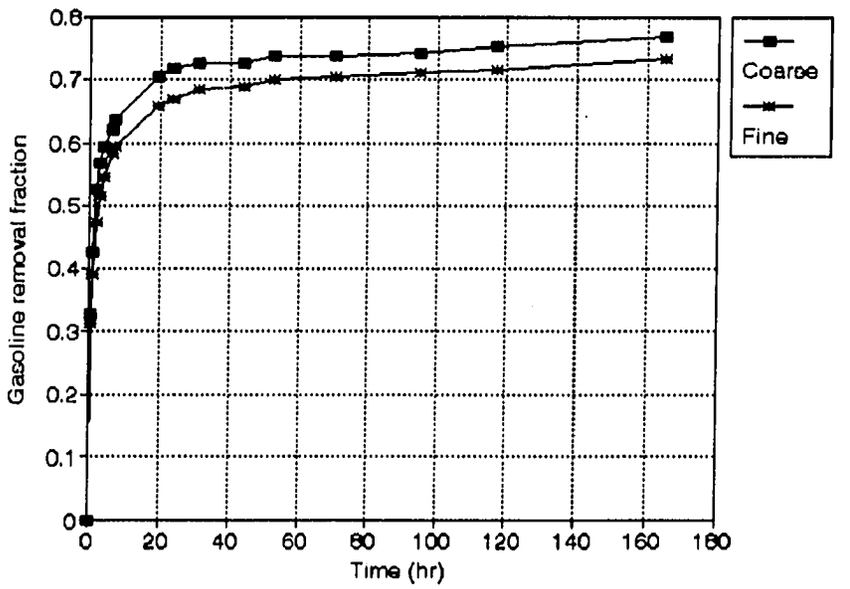


(a)

Figure 5.4. The effect of particle size on the volatilization; duplicate; Aluminum dish was used; "coarse" represents the removed fraction of coarse sand; "fine" represents the removed fraction of fine sand; (a) initial concentration = 0.003 g gasoline/g dry sand; (b) initial concentration = 0.007 g gasoline/g dry sand; (c) initial concentration = 0.010 g gasoline/g dry sand



(b)



(c)

Figure 5.4. (continued)

0.01 g gasoline/g dry sand, respectively. There was a negligible difference in volatilization with respect to particle size.

Another set of experiments was conducted to observe the effect of particle size on the volatilization of gasoline through a dry sand cap. Gasoline was poured into two aluminum dishes and the coarse and the fine sand were immediately poured over them. The fraction of the total gasoline removed by volatilization is shown on Figure 5.5. Again, the differences in volatilization were negligible.

5.3 The Effect of Initial Concentration of Petroleum Products on the Volatilization

The effects of initial concentration of gasoline on volatilization was investigated over a broad range of concentration. Figure 5.6 (a) and 5.6 (b) show the results for experiments conducted using aluminum dish as the weighing vessels with relatively low concentrations and high concentrations of gasoline, respectively. Figure 5.6 (c) shows the results for experiments conducted using 25 ml graduated cylinder as the weighing vessels at relatively high concentrations of gasoline. It was shown from Figure 5.6 that there is linear relationship between initial concentration of gasoline and the amount of gasoline volatilized regardless of the type of weighing vessels. The terminal amount of gasoline volatilized has been plotted in Figure 5.7 as a function of the initial concentration of gasoline the relation between initial concentration and amount volatilized is reasonably linear.

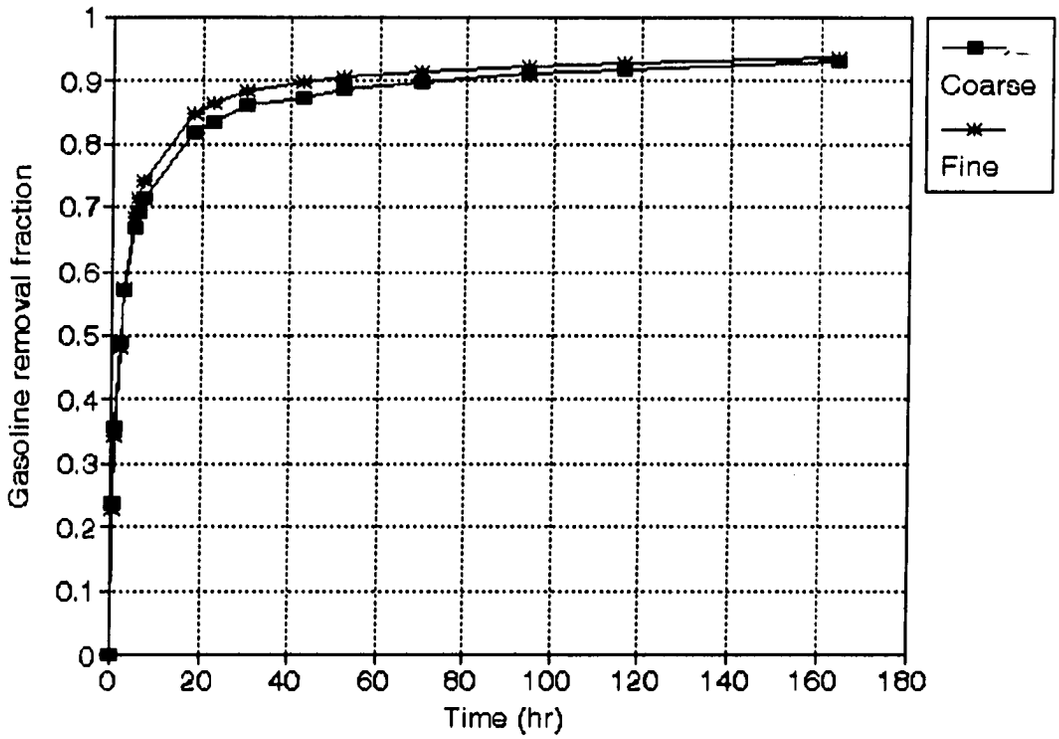
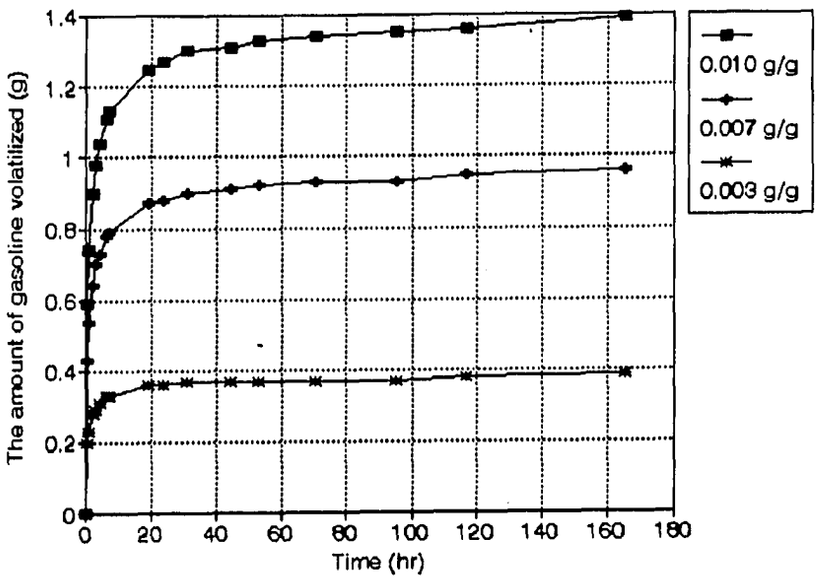
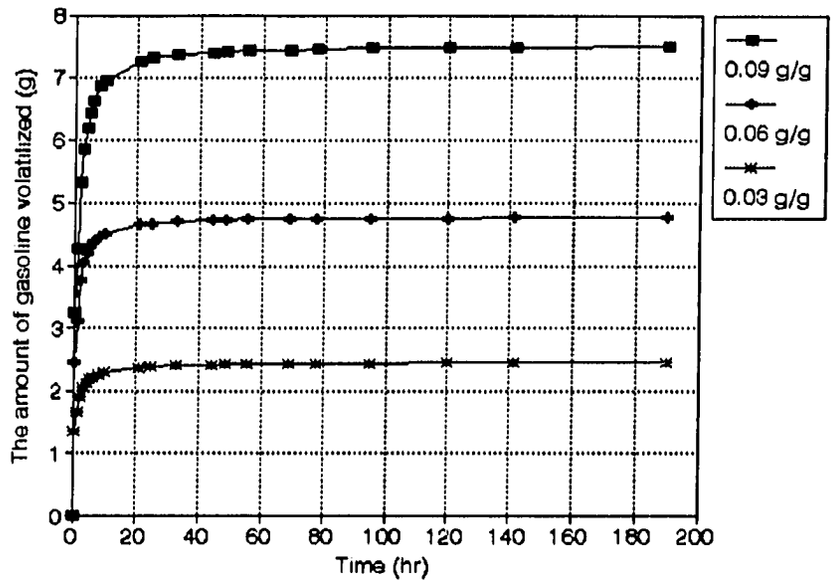


Figure 5.5. The effect of particle size on volatilization; duplicate; aluminum dish was used; initial concentration = 0.01g gasoline/g dry sand; liquid gasoline was poured in bottom and dry sand was poured above that gasoline

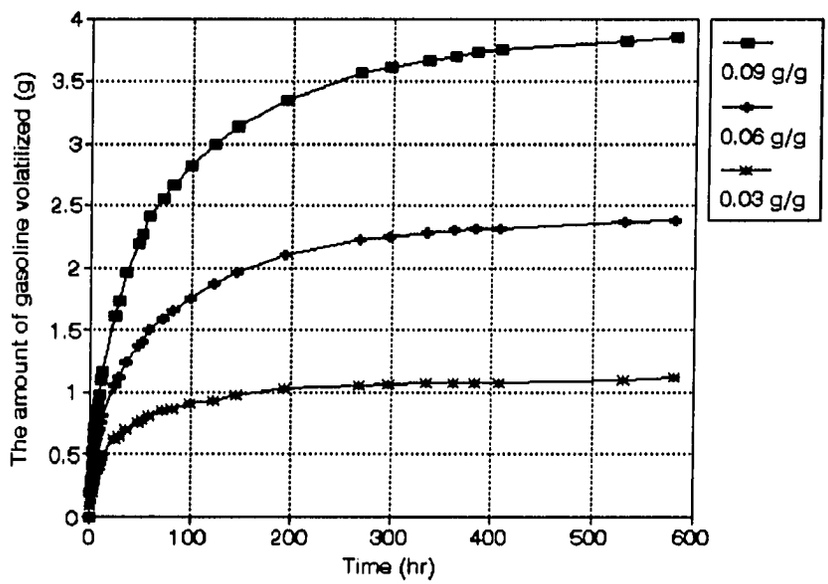


(a)

Figure 5.6. The effect of initial concentration of gasoline on volatilization; single data data; (a) at lower concentration (0.003, 0.007, 0.010 g gasoline/g dry sand), aluminum dish; (b) at higher concentration (0.03, 0.06, 0.09 g gasoline/g dry sand), aluminum dish; (c) at higher concentrations (0.03, 0.06, 0.09 g gasoline/g dry sand), 25 ml graduated cylinder

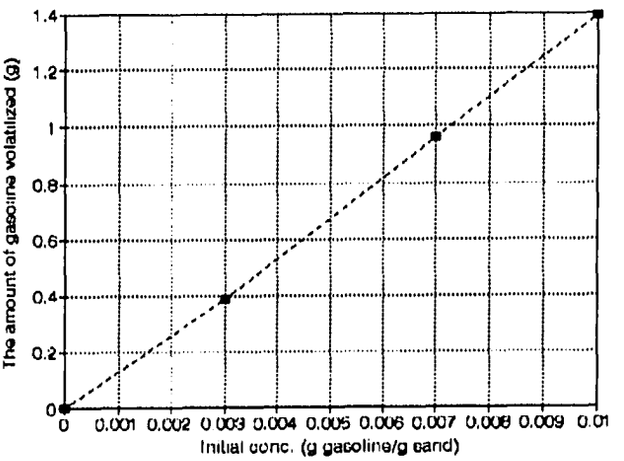


(b)

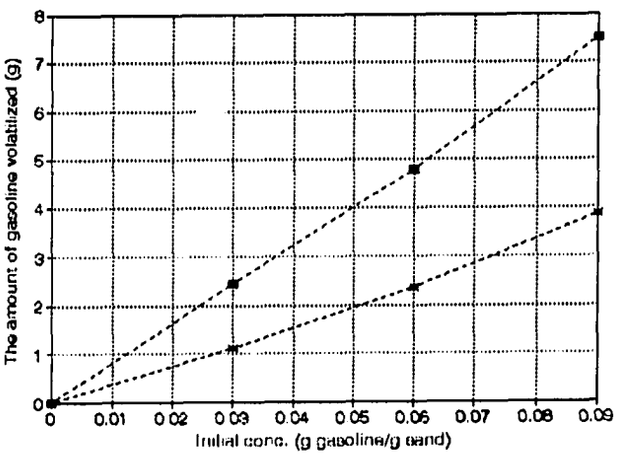


(c)

Figure 5.6. (continued)



(a)



(b)

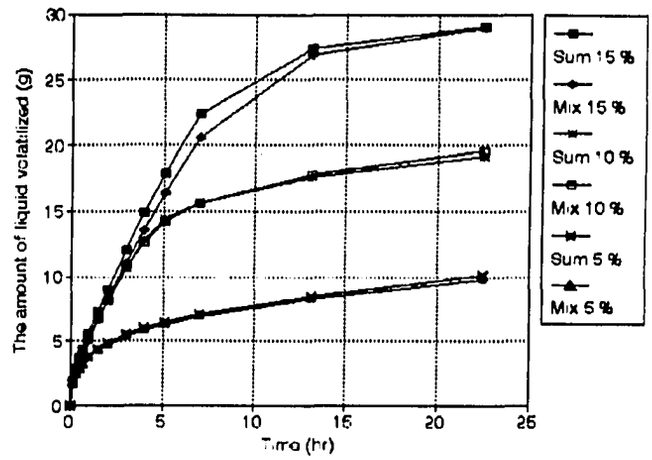
Figure 5.7. Linear relationship between initial concentration and the volatilized amounts of gasoline when there is no more volatilization of gasoline (a) lower concentrations of gasoline, (b) higer concentrations of gasoline; ▪ represents experimental data with aluminum dish; * represents experimental data with 25 ml cylinder

5.4 The Effect of Moisture Content on the Volatilization

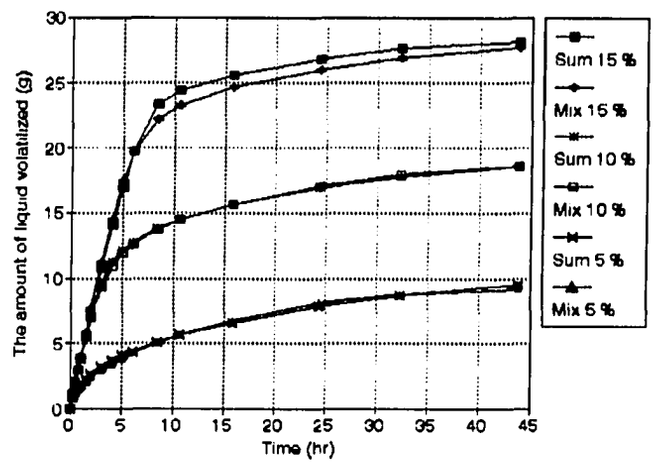
Three different moisture contents (5, 10, and 15 percent based on the weight of the dry sand) were used in testing the effects of moisture content on volatilization. The amount of gasoline used was 3 percent based on the weight of dry sand as was noted previously. Tests were conducted using aluminum dishesas weighing vessels. The results are shown in Figure 5.8. "Mix 5 %" shown in legend stands for the amount of fuel and water from sample which contained a mixture of 5 percent water and 3 percent fuel. "Sum 5 %" shown is legend represents the sum of the amount of fuel and water volatilized at the corresponding times from the sand + fuel and the sand + water samples. That is, "Sum 5 %" was the sum of the amount of fuel volatilized from the sample that initially contained sand containing 3 percent fuel and the amount of water volatilized from the sample initially contained sand containing 5 percent water.

During transferring, initial amounts of mixtures differed from sample to sample. Therefore, some normalization was done. Normalization was done to adjust the amounts of volatilization to the same amount of dry sand weight. There was practically no difference in the amount of liquid volatilized for the mixtures and the sums regardless of the moisture contents.

Therefore, it can be concluded that with up to 15 percent of moisture content, water in the mixture of dry sand, water and fuel did not affect the volatilization of gasoline or diesel fuel. It was also found that the amount of liquid volatilized began to level off after about 12 hours and was proportion to the amount of water added. Therefore, for moisture contents up to at least 15 percent the water did not seem to affect the volatilization of fuel in the mixture.



(a)



(b)

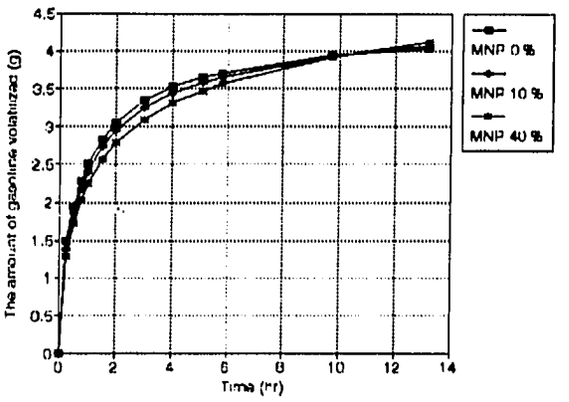
Figure 5.8. Moisture content effect on volatilization; single data; aluminum dish was used; "sum" represents the volatilized amount of fuel plus the volatilized amount of water from samples which were prepared separately; "mix" represents the volatilized amount of fuel and water from sample which was prepared as a mixture of fuel and water; the concentration of fuel was constantly 3 percent; For example, "mix 5 %" represents the amount of fuel and water from sample which was mixture of 5 % water and 3 % fuel; (a) gasoline as fuel; (b) diesel as fuel

5.5 The Effects of Organic Matter on the Volatilization

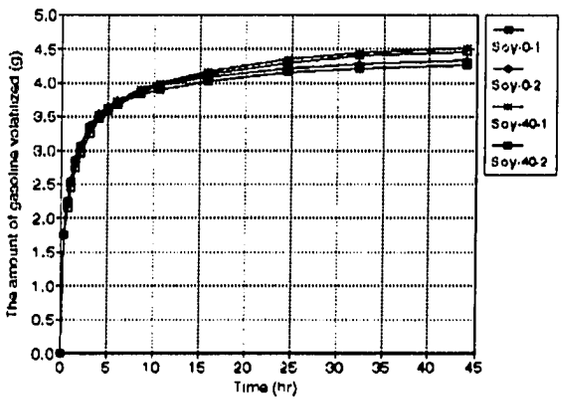
Supposedly, organic matter is able to "wick up" fuel from sand. A series of tests were run to determine whether the addition of MNP or soy hulls would slow down the volatilization of gasoline. The amounts of gasoline volatilized with and without MNP and soy hulls were compared using aluminum dishes as the weighing vessels (Figure 5.9). The amounts of fuel volatilized was normalized based on the same weights of dry sand. It was concluded that the existence of MNP and soy hulls did not effect the volatilization of gasoline in the mixture.

Another set of experiments was run to more investigate the effects of organinc matter on the volatilization of petroleum products. In these tests, sand was not used. Aluminum dishes were used as weighing vessels in these tests. The added amounts of fuel and water were 50 percent of dry weight of organic matter. The results in Figure 5.10 (a) show the effect of MNP on gasoline and diesel and in Figure 5.10 (b) the effect of soy hulls on gasoline and diesel fuel. "Mix" in the legend stands for the amount of fuel and water volatilized from samples prepared using a mixture of water and fuel. "Sum" in the legend stands for the sum of the amount of fuel and water from samples prepared containing water without fuel and fuel without water.

The amounts of liquid volatilized from "Mix" and "Sum" were almost the same for gasoline and diesel with either soy hulls or MNP. That suggests that gasoline and water in mixture did not react with each other. Therefore, there was not a significant effects of organic matter on the volatilization of petroleum products. The absolute amount of liquid for "Mix(Gasoline)" and "Sum(Gasoline)" samples were higher than the absolute amount of liquid for "Mix(Diesel)" and "Sum(Diesel)" samples because gasoline is more volatile

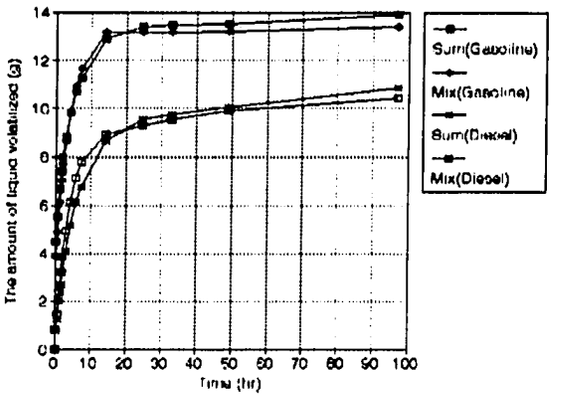


(a)

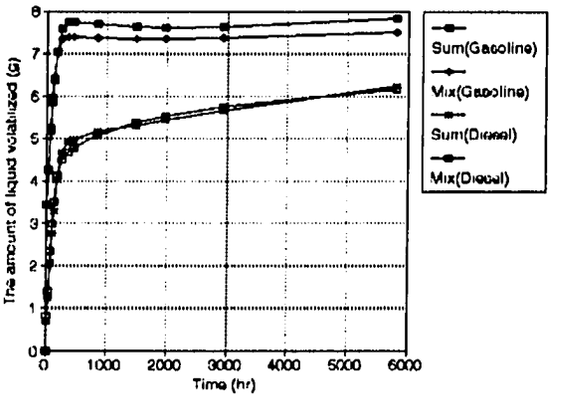


(b)

Figure 5.9. Organic matter's effect on the gasoline volatilization; aluminum dish was used; (a) MNP as organic matter; single data; "MNP 0 %" represents the volatilized amount of gasoline without MNP addition; "MNP 10 %" represents the volatilized amount of gasoline with the addition of 10 % MNP based on the dry sand weight; "MNP 40 %" represents the volatilized amount of gasoline with the addition of 40 % MNP, (b) soy hulls as organic matter; duplicate; "Soy-0-1" represents the first one of duplicates for the sample without soy hulls addition; "Soy-0-2" represents the second one of duplicates for the sample without soy hulls addition; "Soy-40-1" represents the first one of duplicates for the sample with the addition of 40 % soy hulls based on the dry sand weight; "Soy-40-2" represents the second one of duplicates for the sample with the addition of 40 % soy hulls based on the dry sand weight



(a)



(b)

Figure 5.10. Organic matter's effect on the volatilization; single data; aluminum dish was used; sand was not used; added amount of fuel and water were 50 % of dry weight of organic matter, respectively; "Sum(Gasoline)" represents the volatilized amount of gasoline plus the volatilized amount of water from samples which were prepared separately; "Mix(Gasoline)" represents the volatilized amount of gasoline and water from sample which was prepared as a mixture of gasoline and water; "Sum(Diesel)" represents the volatilized amount of diesel plus the volatilized amount of water from samples which were prepared separately; "Mix(Diesel)" represents the volatilized amount of diesel and water from sample which was prepared as a mixture of diesel and water; (a) MNP as organic matter; (b) soy hulls as organic matter

than diesel and there was no interaction between gasoline, water, and either MNP or soy hulls.

5.6 Interactions between Water, Petroleum Products, and Sand Particles

The results of the experiment for interactions between water, petroleum products, and sand particle are summarized in Table 5.2. They show that 1 ml of gasoline was replaced by water in the first experiment where gasoline coated the sand first and water was later. On the other hand, no water was replaced with gasoline in the second experiment where water coated sand first and gasoline was added later.

These results can be explained in terms of polar properties of water and sand particle and non-polar properties of the gasoline. Since both water and sand are polar, water can displace the non-polar gasoline that coated the sand in the first experiment. In the second experiment the water coating the sand was not displaced by gasoline.

Table 5.2. Summary of experiment for interactions between water, petroleum products and sand particle

Set No. of experiment	1st experiment	2nd experiment
Order of addition	Gasoline → Water	Water → Gasoline
Volume of gasoline	1 ml	75 ml
Volume of water	75 ml	0 ml

6. MODELING

In analyzing losses of petroleum products due to volatilization, the fate of petroleum products in contaminated soil, two models were used. One model was based on a heat flow analogy (Thomas, 1982; Mayer *et al.*, 1974) and the other was a material balance model adapted from earlier concepts relating to the Arnold diffusion cell. The experiments described in section 5.1 suggest that the sand appeared to be drying out from the top down. The experiments described in section 5.2 suggest that the particle size of the sand did not play a significant role in the volatilization of fuel in the sand. The material balance model was to designed to incorporate these concepts.

6.1 Heat Flow Model

The model developed by Mayer *et al.* provides a mathematical basis for predicting volatilization of petroleum products as a diffusion-controlled process. It was based on a heat flow analogy and will be referred to in what follows as a heat flow model. The basic assumption in the mathematical treatment of the movement of petroleum products in soils under a concentration gradient is the applicability of the diffusion laws. The changes in petroleum product concentration within the soil as well as the loss of petroleum product at the soil surface by volatilization can then be predicted by solving the diffusion equation for different boundary conditions. By using the analogy between the heat transfer equation (Fourier's law) and the transfer of material under a concentration gradient (Fick's law),

solutions of the heat transfer equation given by the mathematical theory of conduction of heat were used. The analogy between the temperature and the concentration is shown in Figure 6.1. The mathematical model for predicting volatilization of petroleum products was then provided with a set of boundary conditions sufficient to solve the diffusion equation.

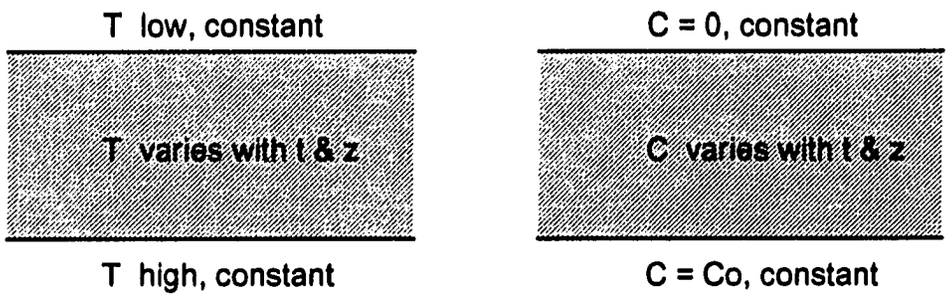


Figure 6.1. The analogy between the temperature and the concentration
T is temperature; C is concentration; t is time; z is depth

The following was assumed:

1. petroleum product is uniformly mixed with a layer of soil and volatilization occurs at the soil surface,
2. diffusion is the only mechanisms transporting petroleum product to the surface,
3. the soil is isotropic, and
4. the diffusion coefficient, D, is constant.

Under these assumptions, the general diffusion equation becomes

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D}\frac{\partial c}{\partial t} = 0 \qquad (6.1)$$

where c = the petroleum product concentration in the soil (g/cm^3 total volume),

x = the distance measured normal to the soil surface (cm),

D = the diffusion coefficient (cm^2/sec), and

t = the time (sec).

Five different solutions were presented by Mayer *et al.*, each applicable to a different set of boundary conditions. Among the five solutions, models 1 and 2 are most applicable to the experimental conditions in the current study.

6.1.1 Model 1

In this model it was assumed that the compound volatilizes and is removed rapidly from the soil surface, maintaining a zero concentration at the surface. The flux at any time depends only on the diffusion coefficient, which must remain constant over the time period of interest. No diffusion occurs across the lower boundary. The boundary conditions were:

$$c = c_O \quad \text{at } t = 0, \quad 0 \le z \le L$$

$$c = 0 \quad \text{at } z = 0, \quad t > 0$$

$$\frac{\partial c}{\partial z} = 0 \quad \text{at } z = L$$

The solution of the diffusion equation with these boundary conditions is

$$c(z,t) = \frac{4c_o}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} e^{-D(2n+1)^2 \pi^2 t/4L^2} \cos \frac{(2n+1)\pi(L-z)}{2L} \tag{6.2}$$

and the flux is given by

$$f = \frac{Dc_o}{\sqrt{\pi Dt}} [1 + 2\sum_{n=1}^{\infty} (-1)^n e^{-n^2 L^2/Dt}] \tag{6.3}$$

6.1.2 Model 2

The summation term in Equation 6.3 will be small if the expression in the exponential, $n^2 L^2 / Dt$, is large. With increasing L and decreasing D or t, the flux becomes:

$$f = \frac{Dc_o}{\sqrt{\pi Dt}} \tag{6.4}$$

or

$$f = c_o \sqrt{D/\pi t} \tag{6.5}$$

The concentration in the soil column for the same boundary conditions as in Model 1 can be expressed as

$$c(z,t) = c_o \text{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \tag{6.6}$$

where "erf" is the error function. The values for error function are shown in Table 6.1.

6.2 Material Balance Model

The material balance is based on the hypothesis that the sand is drying out from the top down. Petroleum products are carried away through the dried out zone by diffusion. At the level where free product exists in the sand, the vapor is saturated. At the surface of the sand, the flow of air maintains a vapor concentration near zero.

The diffusion of liquid gas through a stagnant gas film is well established (Welty *et al.*, 1984; Hines and Maddox, 1985). Diffusion of gasoline through a stagnant air film in an Arnold diffusion cell is shown in Figure 6.2. The vapor gradient of gasoline in the Arnold diffusion is shown in Figure 6.3. The vapor gradient can be assumed to be linear from the saturated value (Co) at the surface of gasoline free product to zero at the top of an Arnold diffusion cell where the air flow sweeps away the gasoline vapor. The gasoline vapor gradient in the soil is assumed in the material balance model to change in the same way (Figure 6.4).

It was shown in section 5.1 that the sand seemed to dry out from the top down as gasoline was volatilized. As gasoline is removed by volatilization, the level at which free product (liquid) is found recedes and the vapor gradient of gasoline decreases. Therefore, gasoline volatilzes at slower rate as time elapses. The vapor gradients of gasoline and diesel fuel in the soil at the saturated concentrations are compared in Figure 6.5. The

Table 6.1. The error function (erf)

ϕ	erf ϕ	ϕ	erf ϕ
0	0.0000	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4284	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

Reference: (Thomas, 1982)

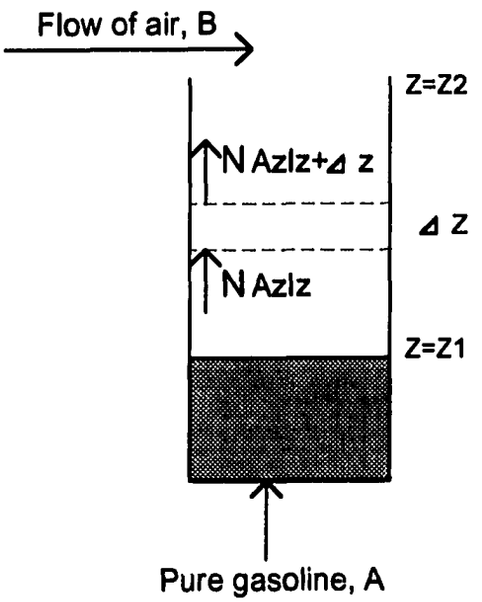


Figure 6.2. Schematic draw of Arnold diffusion cell

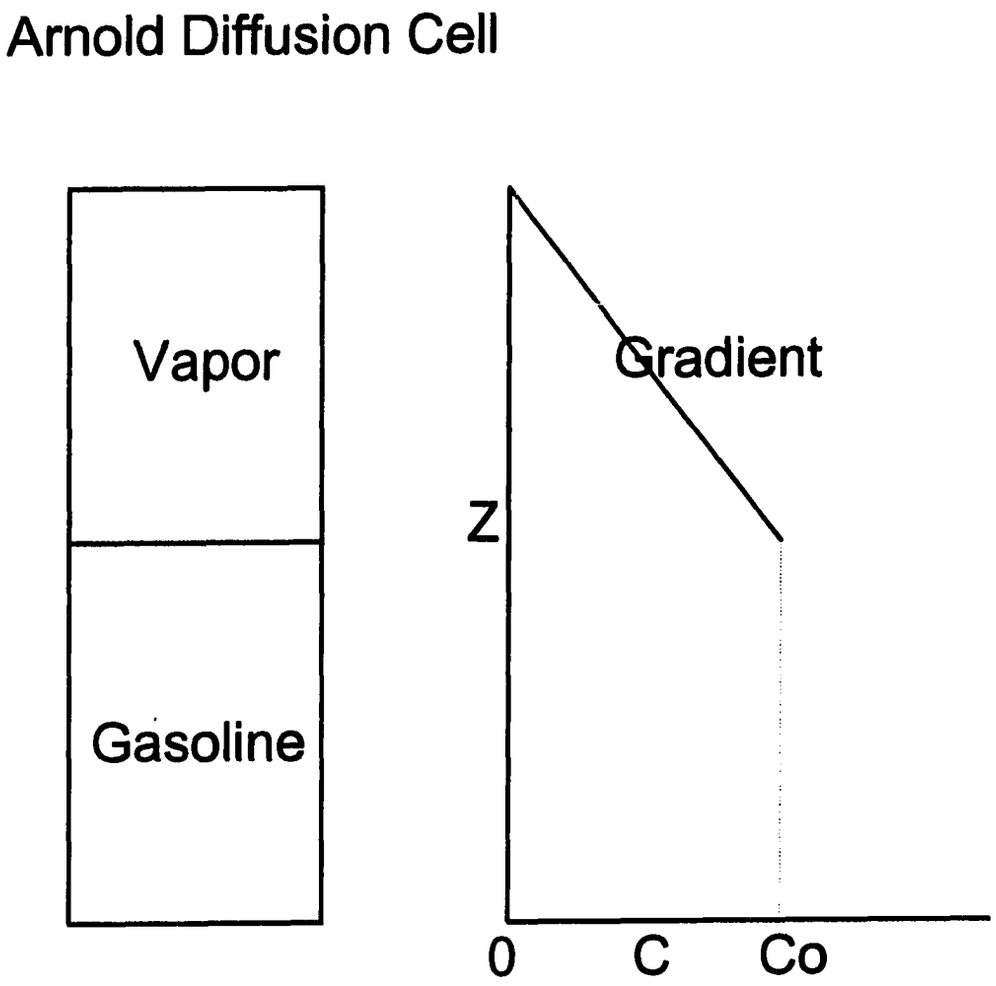


Figure 6.3. The vapor gradient of gasoline in an Arnold cell

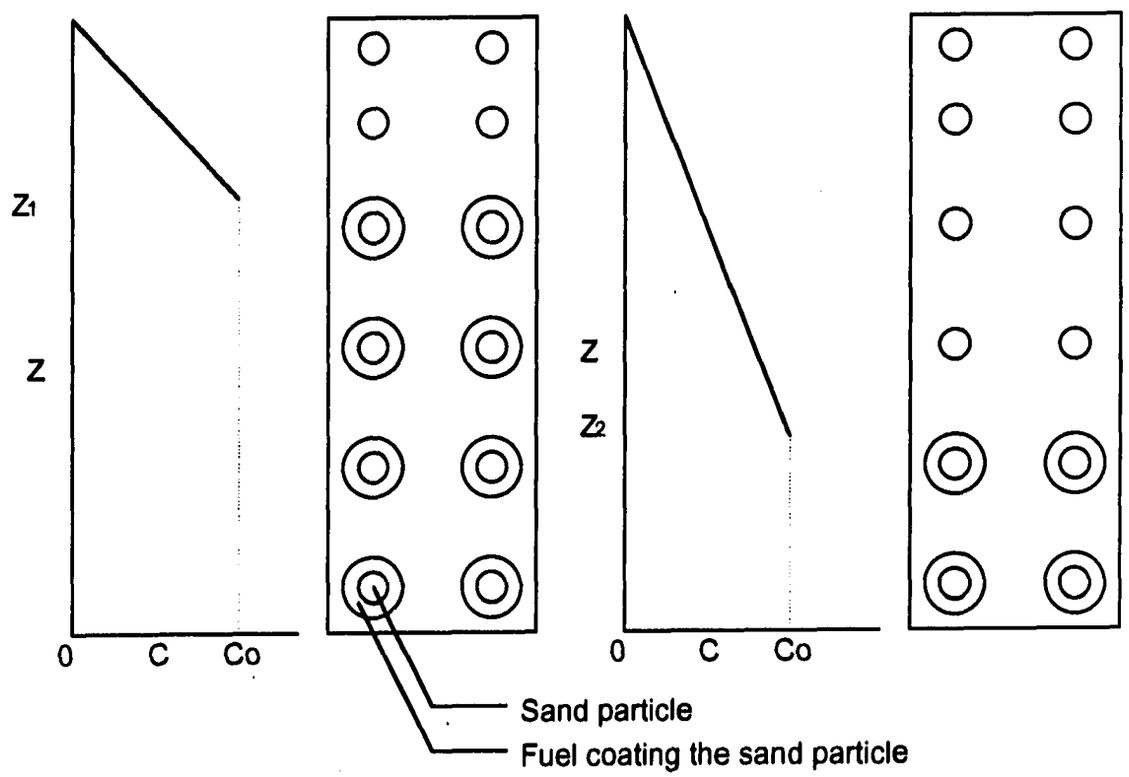


Figure 6.4. The change of gasoline vapor gradient along the volatilizaton of free product; z1 and z2 are the depths from the top to the free product of gasoline

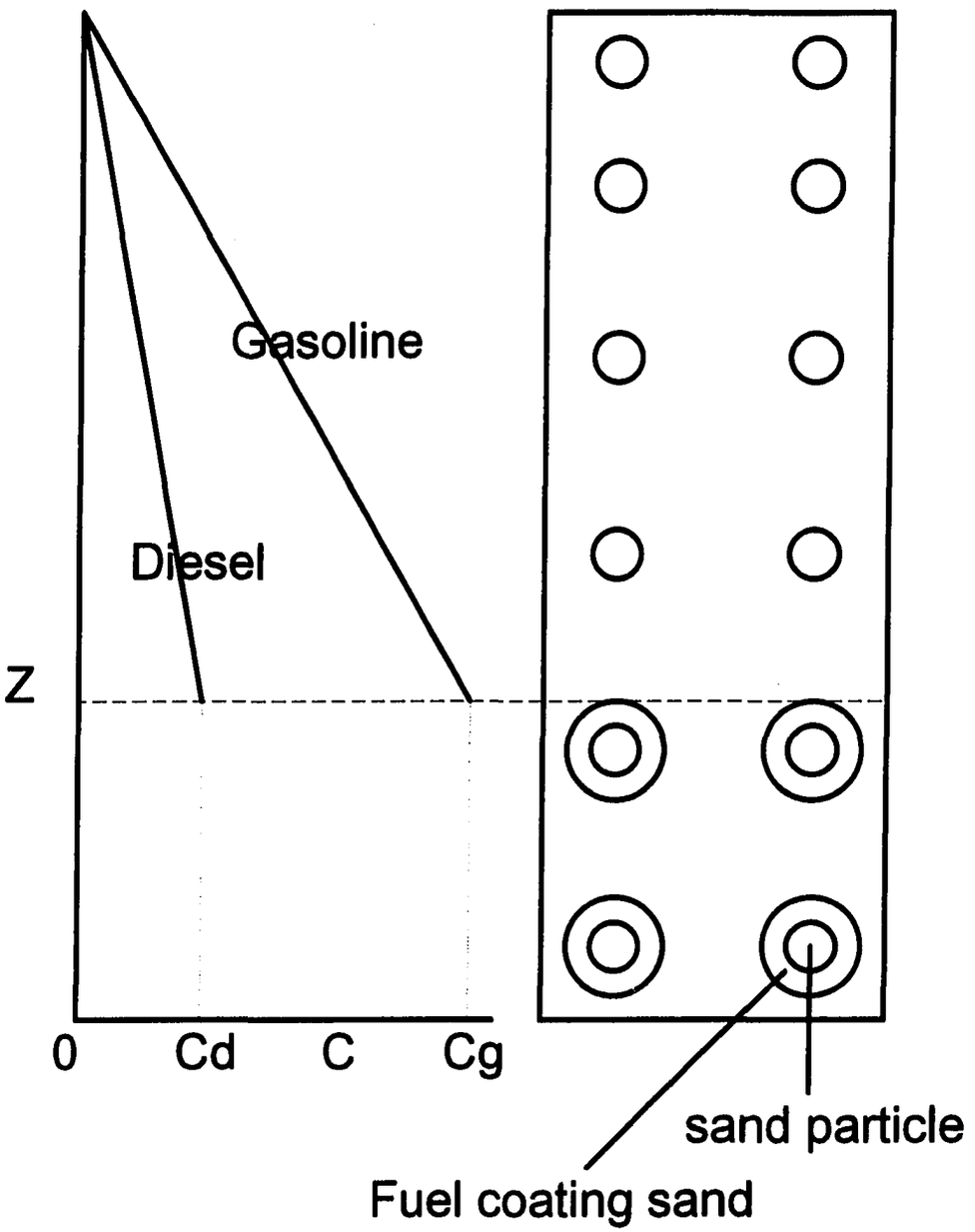


Figure 6.5. The comparison of vapor gradients of gasoline and diesel fuel in the soil; z is the depth from the top; Cd is the saturated concentration of diesel; Cg is the saturated concentration of gasoline

vapor gradients are shown at the same level of free products. The difference in the saturation concentrations is due to the difference in their own volatility. Since gasoline has relatively higher volatility, it has larger vapor gradient compared to diesel fuel.

Consider the diffusion of gasoline through the stagnant air film in an Arnold diffusion cell shown in Figure 6.2. For the control volume $S\Delta z$, a mass balance over control volume for a steady-state condition becomes

$$SN_{A,z}\,|_{z+\Delta z} - SN_{A,z}\,|_{z} = 0 \tag{6.7}$$

where $N_{A,z}$ = the molar flux of component A (gasoline),

S = the cross-sectional area of the tube.

Dividing through by the volume, $S\Delta z$, and as Δz approaches zero, the following equation can be obtained:

$$\frac{d}{dz} N_{A,z} = 0 \tag{6.8}$$

This equation applies to a molar flux of gasoline through the gas phase from z_1 to z_2. A similar differential equation can be generated for component B (air).

$$\frac{d}{dz} N_{B,z} = 0 \tag{6.9}$$

Therefore, the molar flux of component B is also constant over the entire diffusion path from z_1 to z_2. Since component B does not interact with component A, $N_{B,z}$ at z_1 is zero. Therefore, $N_{B,z}$ is zero throughout the diffusion path; that is, the component (air) is a stagnant gas.

The constant molar flux of A was expressed (Welty *et al.*, 1984; Hines and Maddox, 1985) by the equation

$$N_{A,z} = -c_s D_{AB} \frac{dy_A}{dz} + y_A (N_{A,z} + N_{B,z}) \tag{6.10}$$

where c_S = the vapor concentration of component A (gasoline),

D_{AB} = diffusion coefficient of A through B, and

y_A = mole fraction of A in the gas mixture.

This equation reduces, when $N_{B,z} = 0$, to

$$N_{A,z} = -\frac{c_s D_{AB}}{1 - y_A} \frac{dy_A}{dz} \tag{6.11}$$

This equation can be integrated between the two boundary conditions:

at $z = z_1$ $y_A = y_{A1}$

and

at $z = z_2$ $y_A = y_{A2}$

If the diffusion coefficient is constant, the following equation can be obtained by integration.

$$N_{A,z}\int_{z_1}^{z_2} dz = c_s D_{AB}\int_{y_{A1}}^{y_{A2}} -\frac{dy_A}{1-y_A} \tag{6.12}$$

Solving for $N_{A,z}$, we obtain

$$N_{A,z} = \frac{c_s D_{AB}}{(z_2 - z_1)} \ln \frac{(1-y_{A2})}{(1-y_{A1})} \tag{6.13}$$

If we use the log-mean average concentration of component B, which is defined as

$$y_{B,lm} = \frac{y_{B2} - y_{B1}}{\ln(y_{B2} / y_{B1})} \tag{6.14}$$

or, in the case of a binary mixture, this equation can be expressed in terms of component A as follows:

$$y_{B,lm} = \frac{(1-y_{A2}) - (1-y_{A1})}{\ln[(1-y_{A2})/(1-y_{A1})]} = \frac{y_{A1} - y_{A2}}{\ln[(1-y_{A2})/(1-y_{A1})]} \tag{6.15}$$

Inserting Equation 6.15 into Equation 6.13, we obtain

$$N_{A,z} = \frac{c_s D_{AB}}{z_2 - z_1} \frac{(y_{A1} - y_{A2})}{y_{B,lm}} \tag{6.16}$$

Equation 6.16 is the flux of gasoline vapor escaping the soil surface.

On the other hand, we can mathematically describe the movement downward of the saturated zone. A schematic diagram is shown in Figure 6.6.

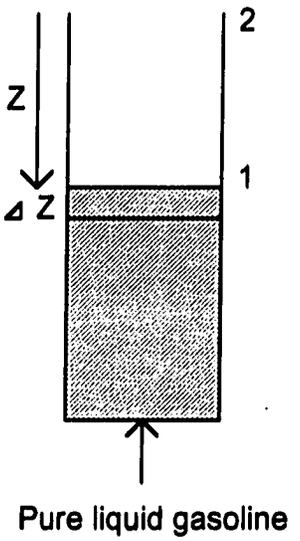


Figure 6.6. Receding level of free product

If we consider the infinitesimal length of tube, ΔZ, filled with gasoline,

$$\frac{\Delta z}{\Delta t} = \text{the velocity of the receding level of free product,} \tag{6.17}$$

$$\frac{A\Delta z}{\Delta t}c = \text{the change in gasoline mass as a fuction of time for } \Delta z\text{, and} \tag{6.18}$$

$$\frac{A\Delta z}{\Delta t}\frac{c}{A} = \text{the flux of liquid gasoline mass for } \Delta z. \tag{6.19}$$

where A = cross-sectional area of tube.

Now, we can equate the Equation 6.16 and Equation 6.19, which becomes

$$\frac{dz}{dt}c = \frac{c_s}{z}\frac{D_{AB}(y_{A1} - y_{A2})}{y_{B,lm}} \tag{6.20}$$

and substituting $\frac{c_s}{c}\frac{D_{AB}(y_{A1} - y_{A2})}{y_{B,lm}}$ by k gives

$$zdz = \frac{c_s}{c}\frac{D_{AB}(y_{A1} - y_{A2})}{y_{B,lm}}dt = kdt \tag{6.21}$$

By integration,

$$\frac{z^2}{2} = kt \quad \text{or}$$

$$z = \sqrt{2k} * t^{1/2} \tag{6.22}$$

Therefore, the flux of gasoline vapor escaping to the surface can be obtained from Equation 6.19 and Equation 6.22; that is,

$$\text{Flux} = \quad c\frac{dz}{dt} = \frac{c\sqrt{k/2}}{\sqrt{t}} \tag{6.23}$$

Substituting for k again gives:

$$\text{Flux} = \sqrt{\frac{c_s c D_{AB}(y_{A1} - y_{A2})}{y_{B,lm}}} / \sqrt{t} \qquad (6.24)$$

Both the heat transfer model and the material balance model were applied to the flux data. Table 6.2 showed the some properties of gasoline, diesel fuel, and the two compounds used to model these fuels.

Table 6.2. Some properties of fuels and model compounds

Substance	D_{air} (cm^2/min)	D_{soil} (cm^2/min)	VP at 25°C (mmHg)	MW	y_{A1}	$y_{B,lm}$	c_S (g/cm^3)
Gasoline	5.2[a]	1.37	258.4[a]	100[a]	0.34	0.824	0.00164
Diesel fuel	2.78[b]	0.73	0.286[d]	202[b]	0.00038	1	0.0033
n-Heptane	3.9	1.03	48.3[c]	100	0.064	0.968	0.00164
n-Dodecane	-	-	0.286[c]	170	0.00038	1	-

[a] Reference: Pedersen and Curtis, 1991
[b] Reference: Shields and Brown, 1989
[c] Reference: CRC Handbook of Chemistry and Physics, 1977
[d] Vapor pressure of *n*-dodecane was used for diesel because no data was available for vapor pressure of diesel fuel and their properties are similar.

The diffusion coefficient, D_{soil}, was calculated from the following equation (Baver *et al.*, 1972):

$$D_{soil} = 0.66\ \varepsilon\ D_{air} \qquad (6.25)$$

y_{A1} was calculated by dividing the vapor pressure of the substance by 760 mmHg. For example, the value for gasoline is 258.4/760 or 0.34. $y_{B,lm}$ was calculated from Equation 6.14 where y_{A2} is set to 0 because the air flow sweeps away the vapor.

The calculation of c_S is based on the ideal gas law:
c_S is equal to P/RT (= 1 atm/(82.06 atm cm^3/mole K)/(298 K) = 4.09*10^{-5} mole/cm^3 empty space). If total volume of soil is considered, 1 cm^3 empty space is equivalent to (1/ε) cm^3 total space. Therefore, c_S is 1.64*10^{-5} mole/cm^3 of total sand volume where ε is 0.4. For example, if the molecular weight of gasoline is 100 g, c_S for gasoline becomes:
c_S = (1.64*10^{-5} mole/cm^3 total sand volume) * (100 g/mole)
= 0.00164 g/cm^3 total sand volume

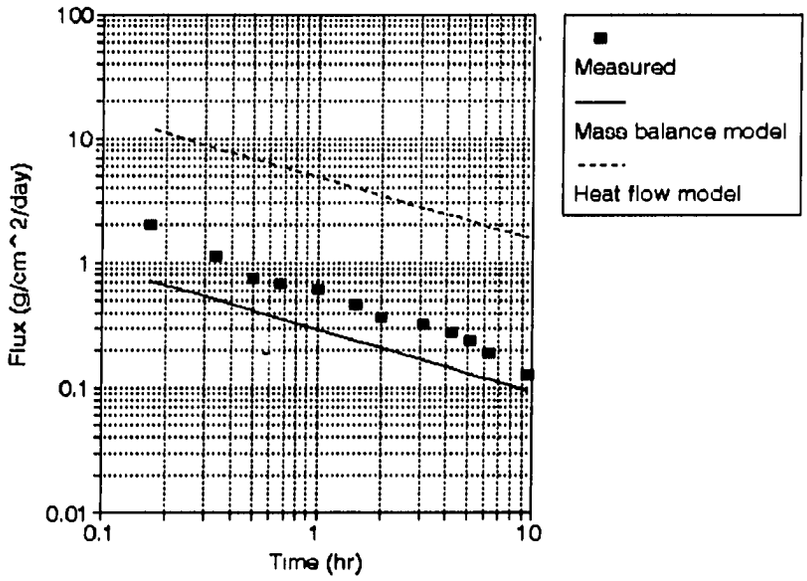
In applying the material balance model, the units for the concentration term, c, should be converted into g fuel/cm^3 total sand volume instead of g fuel/g dry sand. The density of sand particle is 2.65 g/cm^3, which means that 2.65 g of dry sand occupies 1 cm^3 of sand-only volume. Therefore, 1 g of dry sand will occupy 1/2.65 or 0.38 cm^3 of sand-only volume. Since the porosity of sand is 0.4, the total sand volume will be 0.38/0.6 or 0.63 cm^3 of total sand volume. Therefore, 1 g of dry sand is equivalent to 0.63 cm^3 of total sand volume.

n-Dodecane is commonly used as a model compound for diesel fuel in laboratory experiments because its property is similar to that of diesel. Since no data was available for the vapor pressure of diesel fuel, vapor pressure of *n*-dodecane was used for diesel fuel.

To test the applicability of the material balance model to measured data, the material balance model was first tested with *n*-heptane. *n*-Heptane has the constant value for diffusion coefficient whereas gasoline has various values of diffusion coefficient because gasoline is a mixture of hundreds of organic compounds, each having different diffusion coefficients. Moreover, it has the same molecular weight as that of gasoline and it has a similar volatility. The material balance model provided a satisfactory fit to the volatilization data of *n*-heptane but the heat flow model did not (Figure 6.7).

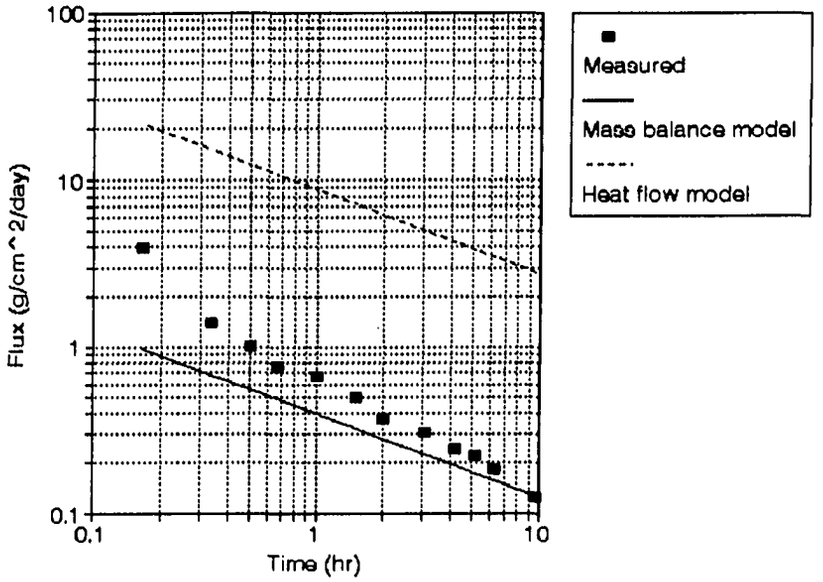
Figure 6.8 shows the results of fitting the heat flow model and the material balance model to gasoline volatilization data at different initial concentration of gasoline in soil mixture. Again, the material balance model fit the data for gasoline much better than the heat flow model. The value of the diffusion coefficient shown in Table 6.2 was used in each model.

Figure 6.9 shows the results of applying the heat flow model and the material balance model to data for the volatilization of diesel fuel. Again, the value for the diffusion coefficient from Table 6.2 was used in both models. The heat flow model did a poor job of modeling the volatilization of diesel fuel. This showed that volatility or vapor pressure is a very important factor in accounting for the volatilization of substances. The diffusion coefficient for diesel fuel is similar to that of gasoline and *n*-heptane (5.2 cm^2/min in air for gasoline, 3.9 cm^2/min in air for *n*-heptane, and 2.78 cm^2/min in air for diesel fuel). However, diesel has relatively very low vapor pressure compared to gasoline and *n*-heptane (258.4 mmHg for gasoline, 48.3 mmHg for *n*-heptane, and 0.286 mmHg for

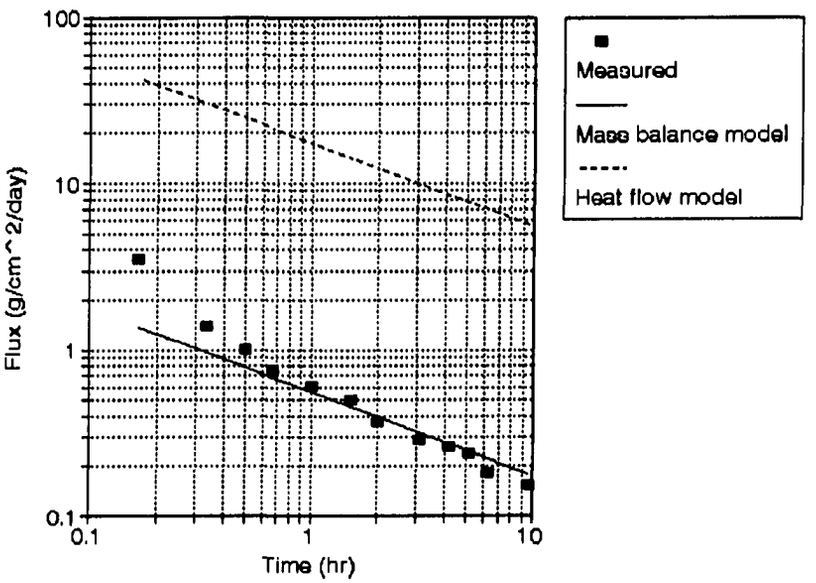


(a)

Figure 6.7. Comparison of models for *n*-heptane; room temperature was 25°C; "Measured" in the legend represents the fluxes of actually measured data(duplicate); (a) initial concentration = 0.03 g *n*-heptane/g dry sand, (b) initial concentration = 0.06 g *n*-heptane/g dry sand, (c) initial concentration = 0.09 g *n*-heptane/g dry sand

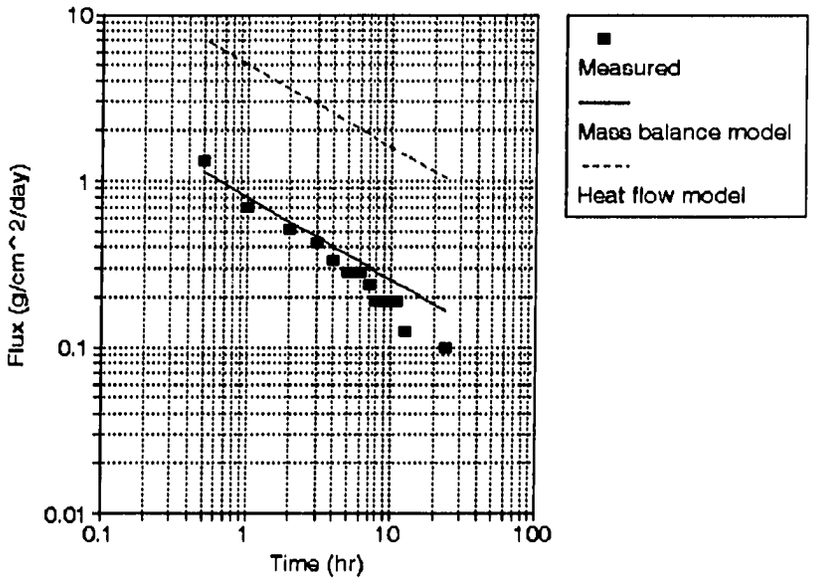


(b)



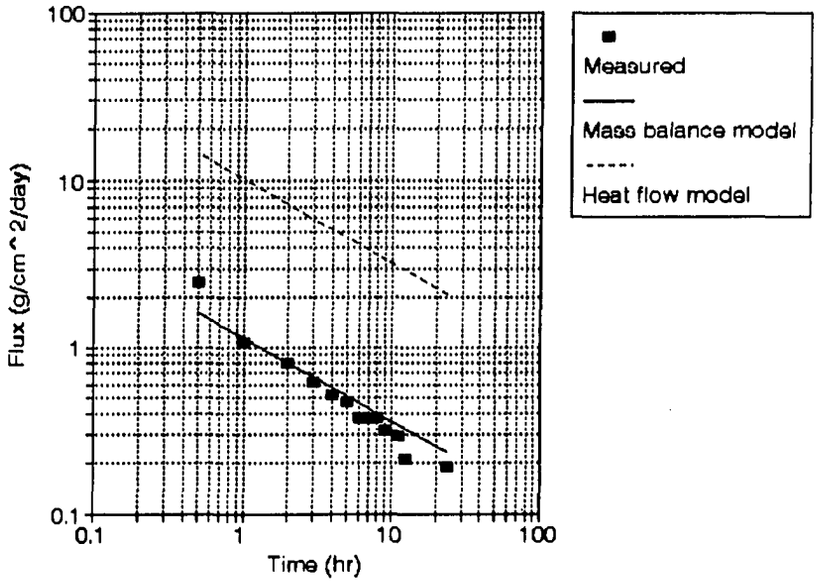
(c)

Figure 6.7. (continued)

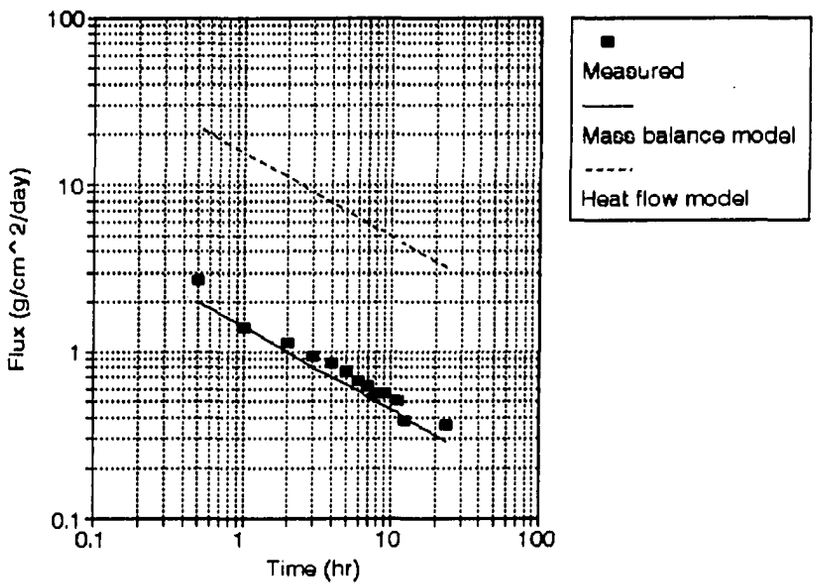


(a)

Figure 6.8. Comparison of models for gasoline; room temperature was 25°C; "Measured" in the legend represents the fluxes of actually measured data(duplicate); (a) initial concentration = 0.03 g gasoline/g dry sand, (b) initial concentration = 0.06 g gasoline/g dry sand, (c) initial concentration = 0.09 g gasoline/g dry sand



(b)



(c)

Figure 6.8. (continued)

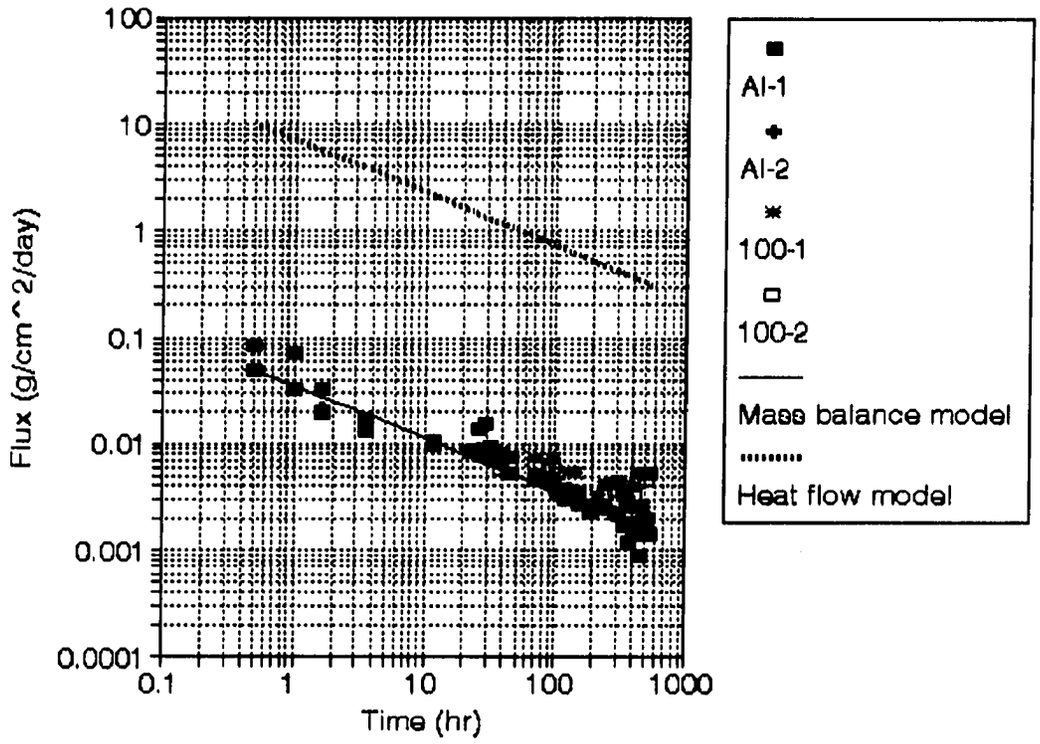


Figure 6.9. Comparison of models for diesel; initial concentration = 0.05 g diesel/g dry sand; room temperature was 25°C; "Al-1" and "Al-2" represent the fluxes from one of duplicate samples using aluminum dish, respectively; "100-1" and "100-2" represent the fluxes from one of duplicate samples using 100 ml graduated cylinder, respectively

diesel). The heat flow model attempts to explain volatilization with only the diffusion coefficients and initial concentrations of substances. It ignores the importance of volatility and therefore fails to fully explain the behavior of volatilization of petroleum products.

Figure 6.9 also demonstrates that the various weighing vessels used in the experiments did not adversely affect the results. Al-1 and Al-2 represented the duplicates of experiment conducted using aluminum dishes as the weighing vessels. 100-1 and 100-2 represented the duplicates of experiment conducted using 100 ml graduated cylinder.

7. CONCLUSIONS

1. Particle size did not significantly affect the volatilization of petroleum product because the porosities of coarser and finer sand were essentially identical for the two particle sizes and the surface characteristics of the sand probably were about the same.

2. The amount of petroleum products volatilized in sand is proportional to the initial concentration of petroleum products in sand mixture up to a concentration of 9 percent based on the weight of dry sand. Therefore, the interaction between the weighing vessels and the petroleum products was probably negligible.

3. Two types of tests were conducted to study the movement of petroleum product in a sand and petroleum product mixture. The first test was used to determine the concentrations of petroleum product at various times and depths. The second test was to determine the flux from contaminated sand capped with different thicknesses of dry sand. Based on these tests, it was concluded that the sand was drying out from the top down.

4. Moisture contents up to 15 percent of the weight of the dry sand did not affect the rate of volatilization of petroleum products from the sand.

5. The addition of MNP and soy hulls to the contaminated sand did not affect the volatilization of petroleum products.

6. The heat flow model did not accurately predict the volatilized flux of petroleum products because it did not consider the effects of product volatility. The material balance model did a good job of predicting the flux of petroleum products from contaminated sand because it incorporated the effects of free product in establishing the concentration gradient for the vapor phase that drives the diffusion process.

BIBLIOGRAPHY

Anderson, T. A., Beauchamp, J. J., and Walton, B. T. (1991). Fate of Volatile and Semivolatile Organic Chemicals in Soils: Abiotic Versus Biotic Losses. J. Environ. Qual., 20, 420-424.

Atkins, P. W. (1986). Physical Chemistry (3rd ed.). New York: W. H. Freeman and Company.

Aurelius, M. W., and Brown, K. W. (1987). Fate of Spilled Xylene as influenced by Soil Moisture Content. Water, Air, and Soil Pollution, 36, 23-31.

Baver, L. D., Gardner, W. H., and Gardner, W. R. (1972). Soil Physics (4th ed.). New York: John Wiley & Sons, Inc.

Blackburn, J. W., and Hafker, W. R. (1993). The Impact of Biochemistry, Bioavailability, and Bioactivity on the Selection of Bioremediation Techniques. Trends in Biotechnology, 11, 328-333.

Bouwer, E. J., and Zehnder, A. J. B. (1993). Bioremediation of Organic Compounds-Putting Microbial Metabolism to Work. Trens in Biotechnology, 11, 360-367.

Call, F. (1957). Soil Fumigation. V.- Diffusion of Ethylene Dibromide through Soils. J. Sci. Food Agric., 8(March), 143-150.

CRC Handbook of Chemistry and Physics (58th ed.). (1977). Ann Arbor, MI: CRC Press, Inc.

Denahan, S. A., Denahan, B. J., Elliott, W. G., Tucker, W. A., and Winslow, M. G. (1990). Relationships Between Chemical Screening Methodologies for Petroleum Contaminated Soils: Theory and Practice. In P. T. Kostecki and E. J. Calabrese (Ed.), Petroleum Contaminated Soils, Vol. 3. (pp. 93-109). Chelsea, MI: Lewis Publishers, Inc.

Donaldson, S. G., Miller, G. C., and Miller, W. W. (1992). Remediation of Gasoline-Contaminated Soil by Passive Volatilization. J. Environ. Qual., 21, 94-102.

EPRI. (1988). Remedial Technologies for Leaking Underground Storage Tanks. Chelsea, MI: Lewis Publishers, Inc.

Frankenberger, W. T., Jr. (1992). The Need for a Laboratory Feasibility Study in Bioremediation of Petroleum Hydrocarbons. In E. J. Calabrease and P. T. Kostecki (Eds.), Hydrocarbons Contaminated Soils and Ground water, Vol. 2. (pp. 237-293). Chelsea, MI: Lewis Publishers, Inc.

Fredrickson, J. K., Bolton, H. Jr., and Brockman, F. J. (1993). *In Situ* and On-Site Bioremediation, E. S. & T., 27(9), 1711-1716.

Gersberg, R. M., Dawsey, W. J., and Bradley, M. D. (1991). Biodegradation of Monoaromatic Hydrocarbons in Groundwater under Denitrifying Conditions. Bull. Environ. Contam. Toxicol., 47, 230-237.

Goodger, E. M. (1975). Hydrocarbon Fuels. New York: John Wiley & Sons, Inc.

Grain, C. F. (1982). Vapor Pressure. In W. J. Lyman, W. F. Reehl, and D. H. Rosenblatt (Eds.), Handbook of Chemical Property Estimation Methods. (pp. 14.1-14.20). New York: McGraw-Hill Book Company.

Hamaker, J. W. (1972). Diffusion and Volatilization. In C. A. I. Goring and J. W. Hamaker (Eds.), Organic Chemical in the Soil Environment, Vol. I. (pp. 341-397). New York: Marcel Dekker, Inc.

Hillel, D. (1971). Soil and Water-Physical Principles and Processes. New York: Academic Press Inc.

Hines, A. L., and Maddox, R. N. (1985). Mass Transfer: Fundamentals and Applications. Englewood Cliffs, NJ: Prentice-Hall, Inc.

Hopper, D. R. (1989). Cleaning Up Contaminated Waste Sites. Chem. Eng., 96, 94-110.

Ince, N., Globus, A. M., and Horton, R. (1992). Simultaneous Soil Heat and Water Transfer. Soil Science, 154(6), 465-472.

Jamison, V. W., Raymond, R. L., and Hudson, J. O., Jr. (1975). Biodegradation of High-Octane Gasoline in Groundwater. Dev. Ind. Microbiol., 16, 305-311.

Jury, W. A., Spencer, W. F., and Farmer, W. J. (1983). Behavior Assessment Model for Trace Organics in Soil: I. Model Description. J. Environ. Qual., 12(4), 558-564.

Karimi, A. A., Farmer, W. J., and Cliath, M. M. (1987). Vapor-Phase Diffusion of Benzene in Soil. J. Environ. Qual., 16(1), 38-43.

Little, C. D., Palumbo, A. V., Herbes, S. E., Lidstrom, M. E., Tyndall, R. L., and Gilmer, P. J. (1988). Trichloroethylene Biodegradation by a Methane-Oxidizing Bacterium. Appl. Environ. Microbiol., 54(4), 951-956.

Lyman, W. J. (1982). Octanol/Water Partition Coefficient. In W. J. Lyman, W. F. Reehl, and D. H. Rosenblatt (Eds.), Handbook of Chemical Property Estimation Methods. (pp. 1.1-1.54). New York: McGraw-Hill Book Company.

McCabe, W. L., Smith, J. C., and Harriott, P. (1985). Unit Operations of Chemical Engineering (4th ed.). New York: McGraw-Hill, Inc.

Mackay, D. (1988). The Chemistry and Modeling of Soil Contamination with Petroleum. In E. J. Calabrease and P. T. Kostecki (Eds.). Soils Contaminated by Petroleum. (pp. 5-18). New York: John Wiley & Sons, Inc.

Mahaffey, W. R., Compeau, G., Nelson, M., and Kinsella, J. (1992). TCE Bioremediation. Water Environment & Technology, February, 48-51.

Mayer, R., Letey, J., and Farmer, W. J. (1974). Models for Predicting Volatilization of Soil-Incorporated Pesticides. Soil Sci. Soc. Amer. Proc., 38, 563-568.

The Merck Index (11th ed.). (1989). Rahway, NJ: Merck & Co., Inc.

Morgan, P., and Watkinson, R. J. (1989). Hydrocarbon Degradation in Soils and Methods for Soil Biotreatment. CRC Critical Reviews in Biotechnology, 8, 305-333.

Nelson, M. J., Kinsella, J. V., and Montoya, T. (1990). In Situ Biodegradation of TCE Contaminated Groundwater. Environmental Progress., 9(3), 190-196.

Nelson, M. J. K., Montgomery, S. O., Mahaffey, W. R., and Pritchard, P. H. (1987). Biodegradation of Trichloroethylene and Involvement of an Aromatic Biodegradative Pathway. Appl. Environ. Microbiol., 53(5), 949-954.

Parr, J. L., Walters, G., and Hoffman, M. (1991). Sampling and Analysis of Soils for Gasoline Range Organics. In P. T. Kostecki and E. J. Calabrese (Eds.),

Hydrocarbon Contaminated Soils and Groundwater, Vol. 1. (pp. 105-132). Chelsea, MI: Lewis Publishers, Inc.

Park, K. S., Sims, R. C., Dupont, R. R., and Doucette, W. J. (1990). Fate of PAH Compounds in two soil types: Influence of Volatilization, Abiotic Loss and Biological Activity. Environ. Toxic. Chem., 9, 187-195.

Pedersen, T. A., and Curtis, J. T. (1991). Soil Vapor Extraction Technology. Rahway, NJ: Noyes Data Corporation.

Plimmer, J. R. (1976). Volatility. In P. C. Kearney and D. D. Kaufman (Eds.), Herbicides: Chemistry, Degradation, and Mode of Action (2nd ed.), Vol. 2. (pp. 891-934). New York: Marcel Dekker, Inc.

Popendorf, W. (1984). Vapor Pressure and Solvent Vapor Hazards. Am. Ind. Hyg. Assoc. J., 45(10), 719-726.

Ridgway, H. F., Safarik, J., Phipps, D., Carl, P., and Clark, D. (1990). Identification and Catabolic Activity of Well-Derived Gasoline-Degrading Bacteria from a Contaminated Aquifer. Appl. Environ.Microbiol., 56, 3565-3575.

Sajjad, M. W. (1992). Biodegradation of Petroleum Products in the Contaminated Soils by SOLV-II, a Modified Natural Product. Unpublished master's thesis, Iowa State University, Ames, IA.

Shieds, W. J., and Brown, S. M. (1989). Applicability of POSSM to Petroleum Product Spills. In P.T. Kostecki and E.J. Calabrese (Eds.), Petroleum Contaminated Soils, Vol I., (pp. 87-104). Chelsea, MI: Lewis Publishers, Inc.

Skladany, G. J., and Metting, F. B., Jr. (1993). Bioremediation of Contaminated Soil. In F. B. Metting, Jr. (Ed.), Soil Microbial Ecology. (pp. 483-513). New York: Marcel Dekker, Inc.

Song, H-G, and Bartha, R. (1990). Effects of Jet Fuel Spills on the Microbial Community of Soil. Appl. Environ. Microbiol., 56(3), 646-651.

Song, H-G, Wang, X., and Bartha, R. (1990). Bioremediation Potential of Terrestrial Fuel Spills. Appl. Environ. Microbiol., 56, 652-656.

Spencer, W. F., and Cliath, M. M. (1990). Movement of Pestcides from Soil to the Atmosphere. In David A. Kurtz (Ed.), Long Range Transport of Pesticides. (pp. 1-16). Chelsea, MI: Lewis Publishers, Inc.

Thibodeaux, L. J. (1979). Chemodynamics. New York: John Wiley & Sons, Inc.

Thomas, J. M., and Ward, C. H. (1989). *In Situ* Biorestoration of Organic Contaminants in the Subsurface. E. S. & T., 23(7), 760-766.

Thomas, R. G. (1982). Volatilization from Soil. In W. J. Lyman, W. F. Reehl, and D. H. Rosenblatt (Eds.), Handbook of Chemical Property Estimation Methods. (pp. 16.1-16.50). New York: McGraw-Hill Book Company.

Troeh, F. R., Jabro, J. D., and Kirkham, D. (1982). Gaseous Diffusion Equations for Porous Materials. Geoderma, 27, 239-253.

Wagenet, R. J., and Rao, P. S. C. (1990). Modeling Pesticide Fate in Soil. In H. H. Cheng (Ed.), Pesticides in the Soil Environment: Processes, Impacts, and Modeling. (pp. 351-399). Madison, WI: Soil Science Society of America, Inc.

Wang, X., and Bartha, R. (1990). Effects of Bioremediation on Residues, Activity and Toxicity in Soil Contaminated by Fuel Spills. Soil Biol. Biochem., 22, 501-505.

Wang, X., Yu, X., and Bartha, R. (1990). Effects of Bioremediation on Polycyclic Aromatic Hydrocarbon Residues in Soil. E. S. & T., 24, 1086-1089.

Welty, J. R., Wicks, C. E., and Wilson, R. E. (1984). Fundamentals of Momentum, Heat, and Mass Transfer (3rd ed.). New York: John Wiley & Sons, Inc.